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## Canadian Journal of Chemistry

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## GAS-LIQUID CHROMATOGRAPHY OF TERPENES PART II. THE DEHYDRATION PRODUCTS OF $\alpha$ -TERPINEOL<sup>1</sup>

E. VON RUDLOFF

### ABSTRACT

The complex mixture of terpenes obtained on dehydrating  $\alpha$ -terpineol with aqueous oxalic acid was almost completely separated by gas-liquid chromatography (GLC), using rapeseed oil as a new liquid phase. Terpinolene, dipentene,  $\alpha$ - and  $\gamma$ -terpinene,  $\Delta^{2,4(8)}$ -*p*-menthadiene, and 1,8-cineole were identified as the major reaction products; three minor and seven trace constituents were also detected. One of the minor components was *p*-cymene, one an oxide, and the third an unidentified hydrocarbon. The yield of these components after different reaction times was determined by GLC. The initial dehydration gives terpinolene and dipentene in the ratio of approximately 2:1. Terpinolene is isomerized to  $\alpha$ - and  $\gamma$ -terpinene,  $\Delta^{2,4(8)}$ -*p*-menthadiene, and the unidentified hydrocarbon, but not to dipentene. 1,8-Cineole and the other oxide are formed in a reversible reaction. Dehydration of  $\alpha$ -terpineol with several other acidic reagents yielded mixtures of products similar to that obtained with aqueous oxalic acid. With acetic acid or acetic anhydride, however, dipentene was formed preferentially and this reaction appears to proceed via the derived acetate.

### INTRODUCTION

The first comprehensive study of the dehydration of  $\alpha$ -terpineol (I) with acidic reagents was carried out by Wallach *et al.* (1, 2), who fractionated the steam-volatile reaction products by distillation and identified some of the constituents by conversion to known derivatives. In this manner terpinolene (II), dipentene (III),  $\alpha$ -terpinene (IV),  $\gamma$ -terpinene (V), and 1,8-cineole (VI) were obtained by use of aqueous oxalic, sulphuric, or phosphoric acids. Mild conditions favored the formation of terpinolene, whereas longer reaction times gave higher yields of  $\alpha$ -terpinene. In the reaction with fused potassium hydrogen sulphate only dipentene was identified. Reaction with acetic acid containing 2% sulphuric acid caused much resinification, whereas that with aqueous formic acid resulted in little dehydration. Flawitzky (3) found that when optically active  $\alpha$ -terpineol was heated in a sealed tube with excess acetic anhydride, large amounts of limonene (optically active III) were formed. Baeyer (4) used the reaction with aqueous oxalic acid for the preparation of terpinolene (very short reaction time) and  $\alpha$ -terpinene, but it is doubtful whether the pure hydrocarbons can be obtained in this manner (5). Using the same reaction for the preparation of  $\alpha$ -terpinene, Alder and Rickert (6) reported the presence of an unidentified diene, which they thought to be possibly a seven-membered ring compound. O'Connor and Goldblatt (7), in a study of the spectral properties of terpene hydrocarbons, reported the preparation of  $\alpha$ - and  $\gamma$ -terpinene and  $\Delta^{2,4(8)}$ -*p*-menthadiene (VII) and  $\Delta^{3,8(9)}$ -*p*-menthadiene (VIII) by dehydration of  $\alpha$ -terpineol

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followed by high-efficiency fractional distillation of the reaction products, but did not give experimental details for these preparations. Terpinolene was obtained by Petrů (8) in the reaction between  $\alpha$ -terpineol and phthalic anhydride, also using short reaction times.

The products obtained in the above reactions thus appear to be rather complex mixtures of *p*-menthadienes and 1,8-cineole and it is doubtful whether all constituents have been identified. The mixtures have a boiling range from about 173–183° C, and it is very difficult to obtain pure components by fractional distillation, even when high-efficiency columns are used. It is possible that azeotropes are formed (9), and in 1891 Wallach himself (10) wrote: "experience has shown that it is especially difficult to determine the presence of other terpenes (*p*-menthadienes) when these are admixed with  $\alpha$ -terpinene". Obviously, different analytical techniques are required for the analysis of such mixtures and gas-liquid chromatography (GLC) appears to be the ideal tool at the present time.

#### GAS-LIQUID CHROMATOGRAPHIC SEPARATION

Previously (11), the mixture obtained in the reaction of  $\alpha$ -terpineol with aqueous oxalic acid was used by the author as one of the test mixtures in a study of some of the general aspects of the separation of terpenoid compounds by means of GLC. Using 6-ft  $\times$  1/4-in. diameter columns with Craig polyesters, polyethylene glycol, polyphenyl ether, or squalene as liquid phase, it was shown that the mixture was composed of at least seven compounds, but the degree of separation obtained with these columns was insufficient to allow quantitative calculations or qualitative separations for preparative purposes. The investigation was therefore continued in order to find conditions which would permit a satisfactory analysis of this mixture and thus facilitate the study of the dehydration reaction itself.

There are several ways by which the chromatographic separations can be improved (12). Increasing the column length is limited by the dimensions of the apparatus and eventually by excessive retention times. The use of thinner diameter columns and smaller samples (less than the 1 to 20  $\mu$ l commonly used) may also lead to increased efficiency, but requires an exceedingly sensitive detector. A third means of improving the degree of separation is by selecting a more efficient liquid phase. Of the liquid phases used for the separation of terpene hydrocarbons as described in the literature of the past year (9, 13–16), none gave better results for the mixture under consideration than were already obtained previously. In Part I (11) it was shown that squalene was a useful liquid phase and a 12-ft column did indeed give almost complete separation. However, this material is subject to fairly rapid deterioration and cannot be used above 100–120° C for any length of time. It may be reasoned that aliphatic olefins of greater stability and larger molecular weight may give equal or better results. Such compounds are readily available in the form of the triglycerides of vegetable oils, with the added advantage that a wide choice in the degree of unsaturation is available. The additional polarity due to the ester groups would be favorable in this instance, since the polyester columns partially separated peak C into two components whilst the squalene column did not (11). Superior separations were, in fact, obtained when rapeseed or olive oil were used as liquid phase. Oils having a higher degree of unsaturation, e.g. linseed or sunflower seed oil, were not as efficient, a finding which indicates that triolein itself may be very suitable as liquid phase. Columns containing rapeseed or olive oil gave reproducible results during 2 to 3 months of continuous or intermittent use at 120° C or lower, provided they were kept under helium or nitrogen at all times.

A 13-ft rapeseed oil column at 90° C was found to give almost complete separation of

the components of the above mixture of terpenes with reasonable retention times. This allowed the near quantitative determination ( $\pm 2$  to 3%) of the nine components found to be present in the *p*-menthadiene range. Trace components (less than 0.5–1%) were also present in the camphene – *p*-menthene range (three peaks) and in the range between the *p*-menthadienes and unreacted  $\alpha$ -terpineol (four peaks). This column, together with 12-ft polyester and polyethylene glycol and 6-ft polyphenyl ether columns, was used to determine the composition of the steam-volatile products obtained in the dehydration of  $\alpha$ -terpineol.

## EXPERIMENTAL

The gas-chromatographic equipment and procedures were those described previously (11). All columns were made up with the liquid phase on Chromosorb W (60–80 mesh) in the ratio of 1:6 (by weight). The retention times, measured from the time of injection to the initial emergence of a peak, of various terpenes on the columns used are shown in Table I. The percentage composition of a particular mixture was determined by the

TABLE I  
Retention times\* (in minutes) of terpenes on three GLC columns

Compound	Peak No.	13-ft rapeseed oil (90° C, 59 ml He/min)	6-ft polyester (APEG) + 6-ft polyethylene glycol (80° C, 46 ml He/min)	6-ft polyphenyl ether (120 ml He/min)	
				80° C	130° C
$\alpha$ -Pinene	—	43.5	8.6	3.9	—
Camphene	1	55.8	11.4	5.4	1.8
$\beta$ -Pinene	—	58.1	15.1	6.3	—
Oxide 1	2	77.0	22.0	8.5	2.8
$\alpha$ -Terpinene	3	84.7	23.7	8.9	2.9
1,8-Cineole	4	92.4	31.0	12.7	3.6
Dipentene	5	96.5	27.0	10.4	3.1
<i>p</i> -Cymene	6	104.7	31.0	12.7	3.6
$\gamma$ -Terpinene	7	109.6	36.2	14.4	4.2
Unidentified	8	134.8	41.7	17.0	4.7
Terpinolene	9	144.8	45.7	18.6	5.1
$\Delta^{3,4(8)}$ - <i>p</i> -Menthadiene	10	154.7	47.0	18.8	5.1
Unidentified	11	—	—	—	10.4
Unidentified	12	—	—	—	12.2
Unidentified	13	—	—	—	14.2
$\alpha$ -Terpineol	14	—	—	—	16.1
Unidentified	15	—	—	—	18.5
$\alpha$ -Terpinyl acetate	16	—	—	—	30.6

\*Measured from the time of injection to initial emergence of the peaks.

area under the curves. Test runs with a synthetic mixture of pure limonene, 1,8-cineole, and  $\alpha$ -terpineol gave values within  $\pm 1.5\%$  of the weight composition, provided the peaks did not tail. When tailing took place, as with  $\alpha$ -terpineol on some columns, the calculated values were low by 2–3%. Duplicate runs on the same column agreed within 0.5%, but differed on different columns by as much as 3%. Preparative runs (10 to 50 mg) were carried out either on the analytical 1/4-in. diameter columns, or on a combination of a 3-ft  $\times$  3/8-in. diameter silicone grease column used ahead of a 6-ft  $\times$  1/4-in. polyphenyl ether column. Samples were collected with the detector current off (11), and the purity of the fractions collected was determined by injecting 1- to 3- $\mu$ l aliquots into the analytical columns. At no time was there any evidence of decomposition or rearrangement of any of the components isolated. Individual components were identified by infrared and ultraviolet spectra, by retention times, and, where possible, by conversion



to known crystalline derivatives by standard techniques (5, 17) or as indicated. Melting points were determined on a Leitz hot-stage microscope. Infrared and ultraviolet spectra were recorded on Perkin-Elmer Model 21 infrared and Warren Electronic Inc. Spectracord spectrophotometers, respectively, using the film or potassium bromide disk method for the former instrument.

Commercial *dl*- $\alpha$ -terpineol was purified by fractional distillation through a Podbielniak 8-mm diameter spinning band column until GLC analysis showed less than 1% impurities to be present. Thus purified it had  $n_D^{20}$  1.4829 (lit. (17) 1.4813, 1.4832) and gave the phenylurethane, m.p. 112–113° C (lit. (2, 5) m.p. 113° C), in good yield.  $\alpha$ -Terpinyl acetate was prepared by refluxing  $\alpha$ -terpineol with excess acetic anhydride in the presence of sodium acetate for 4 to 5 hours and was purified by fractional distillation;  $n_D^{20}$  1.4666 (lit. (17) 1.4689).

#### *Small-Scale Dehydration Experiments*

$\alpha$ -Terpineol (1.0 g), oxalic acid (hydrate, 4.0 g), and water (5.0 ml) were placed in a 25-ml flask which had two necks with ground-glass joints. A small reflux condenser was attached to one of the joints whilst the other one was tightly stoppered. The mixture was brought to boil and refluxed for the required length of time. The reflux condenser was then changed to the horizontal position and the mixture was steam-distilled for 20 to 30 minutes. The distillate was collected in an ice-cooled flask and, after distillation was complete, the condenser was rinsed with a small amount of ether. The steam-volatile terpenes were recovered by extraction with small amounts of ether, the ethereal solution was washed with bicarbonate solution, then with water, and was dried over anhydrous sodium sulphate. The dried solution was quantitatively transferred to a weighed 25-ml flask having a long neck, and the ether was evaporated on a water bath at 80–90° C. In blank test runs with pure limonene the recovery was 94–98% with 3–5% ether remaining. Calculation of yields and percentage composition were, therefore, based on a 96% recovery. On this basis the yields were 98–100% of theory for reaction up to 8 hours. After that losses due to resinification became marked; for example, after 12 hours, the recovery was only 76% of theory.

In experiments using other dehydrating agents the same procedure was followed. The amounts of reagent used and reaction times are shown in Tables II and III.

#### *Isolation and Identification of Individual Components*

##### *Terpinolene (Peak No. 9)*

Oxalic acid (hydrate, 160 g) and water (200 ml) were brought to boil in a 500-ml flask which was equipped with a condenser, a dropping funnel, and an inlet tube. Steam was passed through the boiling solution and  $\alpha$ -terpineol (40 g) was added dropwise (4), the steam distillate being collected in an ice-cooled flask. After the addition was complete, the mixture was steam-distilled for a further hour. The terpene mixture was recovered as described above. The crude product (38 g) was analyzed by GLC and then fractionally distilled through the spinning band column. The fractions collected were analyzed by GLC. The ninth (3.1 g), b.p. 92.5° at 41 mm Hg pressure, was found to contain better than 90% of peak 9 and had  $n_D^{20}$  1.4914 (lit. (7) 1.4888). The infrared spectrum resembled that reported for terpinolene (7). The ultraviolet absorption was weak and devoid of any characteristic band due to conjugation. The fraction gave in good yield a crystalline bromide, m.p. 112–115° C, recrystallized from ether-methanol, m.p. 115.0–115.8° C (lit. (2) m.p. 116° C). Found: C, 26.48%; H, 3.68%; Br, 70.24%. Calculated for  $C_{10}H_{16}Br_4$ : C, 26.34%; H, 3.54%; Br, 70.12%. The derived tetrol was prepared as follows: terpinolene (126 mg) was added to an ice-cold solution of tertiary butanol (10 ml) and water (10 ml)

TABLE II  
Yield of steam-volatile products in the reaction with  $\alpha$ -terpineol (1.00 g)

Reagent	Reagent (ml)	Reaction time (hr)	Total yield (g)	Percentage of individual components in volatile product													
				1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sulphuric acid (33%)	4	1	0.85	—	1.5	28.5	5	9	6	15	1	18.5	15	—	—	—	—
Phosphoric acid (20%)	4	1	0.98	—	3	7.5	3	7.5	2.5	6	—	11	1.5	—	—	—	—
Phosphoric acid (20%)	4	4	0.88	—	4.5	10	2	8	4	8	—	12.5	3	3.5	1.5	4.5	49
Acetone-H <sub>2</sub> SO <sub>4</sub> (20%)	2+5	1	0.85	—	3	9	4	4	—	7.5	—	8.5	2.5	4	1	6	38
Ethanol-H <sub>2</sub> SO <sub>4</sub> (98%)	4+1	1	0.43	16	1	27	3	5	5	13	1	8	6.5	3.5	—	3.5	4
KHSO <sub>4</sub> anh.	(2 g)	1	0.86	—	1	19	4	16	5.5	15.5	—	31	6	—	—	—	—
KHSO <sub>4</sub> anh. (pyro)	(3 g)	1	0.64	11	6	2	75	—	3	—	—	2	—	—	—	—	—
Phthalic anhydride	(2 g)	1	0.54	6.5	4.5	27	10	8.5	8	13	—	19	1	—	—	—	—
Acetic anhydride	5	16	1.02	—	1	3	1	32	1.5	3	—	6	—	—	—	3.5	50
Acetic acid (98%)	5	12	0.94	—	—	0.5	1.5	16	0.5	0.5	—	6	—	—	—	69.5	5
Acetic acid (50%)	5	2	0.95	—	—	0.5	1	5.5	—	—	—	6.5	—	—	0.5	1.5	—
Acetic acid (50%)	5	6	0.94	—	—	1.5	3	10.5	1	1.5	—	12	3	1.5	2	3	58.5
Acetic acid (50%)	5	18	0.75	—	3	10	9	15	4	11	—	29	3	1.5	1.5	2	8
Acetic acid + H <sub>2</sub> SO <sub>4</sub> (5%)	5	12	0.21	18	5	2	37	1	0.5	0.5	—	1	—	—	—	—	32
Acetic acid + H <sub>2</sub> SO <sub>4</sub> (5%)	5	3*	0.34	7.5	12.5	—	24	4	22	—	—	1	0.5	—	—	—	26
Formic acid (98%)	4	6	0.14	13	8	—	24	—	10	—	—	1.5	—	—	—	3	31.5

\*At room temperature.

TABLE III  
Yield of steam-volatile components in the reaction with  $\alpha$ -terpinyl acetate (1.00 g)

Reagent	Reagent (ml)	Reaction time (hr)	Total yield (g)	Percentage of individual components in volatile product													
				1	2	3	4	5	6	7	8	9	10	11	12	13	14
Acetic acid (98%)	5	18	0.56	—	—	1.5	0.5	46	—	2.5	—	21.5	—	—	—	—	4
Acetic acid + H <sub>2</sub> SO <sub>4</sub> (5%)	5	3*	0.29	7	9	8	30	3	19	10	—	8	—	—	—	—	29
Acetic acid + H <sub>2</sub> SO <sub>4</sub> (5%)	5	18*	0.18	12	6	2	27	2	18	4	—	5	—	—	—	—	11
Acetic anhydride	5	18	0.98	—	2	3	2	30	1	2.5	—	5	—	—	—	—	20
Acetic anhydride + H <sub>2</sub> SO <sub>4</sub> (5%)	5	18	0.19	2.5	1	0.5	80	—	7	—	—	—	—	—	—	—	18

\*At room temperature.

containing potassium hydroxide (0.1 g). To this was added with vigorous stirring and further cooling finely powdered potassium permanganate (0.4 g) in small aliquots. The initial permanganate color changed to black-purple, then to a dark green, and finally to a muddy brown. After complete addition and stirring for a further 10 minutes, the precipitated manganese dioxide was filtered off and the pH of the filtrate was brought to about 7 by leading in carbon dioxide. The solution was evaporated to dryness and extracted with ethanol:2-butanone (1:1 v/v). The mixture of solvents was evaporated and the residual material (192 mg) was taken up in a small volume of ethyl acetate or 2-butanone. The tetrol crystallized very slowly on keeping the solution at 0–2° C for several weeks. Recrystallization from these solvents was also very slow. Whilst the yield of crude tetrol was very good, that of crystalline material, m.p. 148–150° C (lit. (17) m.p. 149–150° C), was poor. Found: C, 58.71%; H, 9.78%. Calculated for  $C_{10}H_{20}O_4$ : C, 58.80%; H, 9.87%.

An aliquot of fraction 9 was purified by preparative GLC, 10 runs giving 100 mg of almost pure (99.2%) peak 9. It formed the terpinolene bromide in excellent yield and the derived tetrol more readily than the impure fraction.

*Dipentene (Peak No. 5)*

The first five fractions obtained in the above fractional distillation showed a high content of peak 5. These fractions were combined and redistilled to give a middle fraction containing about 80% of peak 5. This was further purified by preparative GLC, giving 98% pure peak 5. Its infrared spectrum corresponded to that of dipentene (7) and both the derived tetrabromide, m.p. 125.0–126.0° C (lit. (2, 17) m.p. 124–126° C) and tetrol, m.p. 191.5–192° C, were obtained in excellent yield. Found for the bromide: C, 26.52%; H, 3.67%; Br, 70.07% and for the tetrol: C, 58.66%; H, 9.84%.

*$\alpha$ -Terpinene (Peak No. 3)*

$\alpha$ -Terpineol (40 g) was refluxed with a mixture of oxalic acid (hydrate, 160 g) and water (200 ml) for 12 hours. The mixture was steam-distilled and the crude hydrocarbon mixture (29 g) recovered as above. Fractions 2 to 4 in the fractional distillation at 36 mm had a boiling point of 77–80° C and GLC analysis showed a high content of peak 3, with minor amounts of peaks 2, 4, 5, and 6 being present. Preparative GLC gave peak 3 in 95–96% purity,  $n_D^{20}$  1.4792 (lit. (7) 1.4778). Its infrared and ultraviolet spectra corresponded to those of  $\alpha$ -terpinene (7). No solid bromide was obtained nor did the permanganate oxidation give a derived tetrol. However, the acidified oxidation mixture on extraction with 2-butanone gave a good yield of  $\alpha,\delta$ -dihydroxy- $\alpha$ -methyl- $\delta$ -isopropyl adipic acid, m.p. 187–188° C (lit. (17, 18) m.p. 188–189° C). Found: C, 51.43%; H, 8.10%; neutral equivalent 115.5. Calculated for  $C_{10}H_{18}O_6$ : C, 51.27%; H, 7.75%; neutral equivalent 117.12. The compound melts with loss of water and forms the dilactone, m.p. 71–73° C, readily (18). The terpene gave the crystalline nitrosite, m.p. 155.5–156.5° C (lit. (2, 17) m.p. 155° C), in good yield.

*$\gamma$ -Terpinene (Peak No. 7)*

Fractions 5 to 7 in the above fractional distillation had a boiling point of 80.5–84.5° C and showed a high content of peak 7. This was purified by GLC, when practically pure peak 7 was obtained;  $n_D^{20}$  1.4748 (lit. (7) 1.4747). Its infrared spectrum was similar to that of  $\gamma$ -terpinene (7). The derived tetrol, m.p. 235–237° C (lit. (18) m.p. 237° C), was obtained in good yield. Found: C, 58.69%; H, 9.81%. This material also gave a crystalline nitroschloride, m.p. 110–111° C, in fair yield.

*$\Delta^2,4(8)$ -*p*-Menthadiene (Peak No. 10)*

The last two fractions in the above fractional distillation contained mainly peak 10

as well as some terpinolene (peak 9). Purification by GLC proved difficult, since these two peaks were not completely resolved. However, a small amount of peak 10,  $n_D^{20}$  1.5030 (lit. (7) 1.5030), was obtained about 92–95% pure. The infrared and ultraviolet spectra ( $\lambda_{\max}$  243 m $\mu$ ) corresponded to those of  $\Delta^{2,4(8)}$ -*p*-menthadiene (7). A nitrosite, m.p. 152–155° C, was obtained in poor yield. Pines and Eschinazi (19) report a melting point of 153–155° C for the  $\beta$ -nitrosite and melting points of 110°, 140–150° C for the  $\alpha$ -nitrosite.

*Oxides (Peaks Nos. 2 and 4) and p-Cymene (Peak 6)*

An aliquot of the terpenoid mixture obtained in the preparation of terpinolene was oxidized exhaustively with cold, aqueous potassium permanganate. The unoxidized terpenes were recovered by extraction with ether. The dried ethereal solution was carefully evaporated and the residual material was analyzed by GLC. Peaks 2, 4, and 6 only were recorded, the major component being peak 4. The latter was isolated 95–96% pure by preparative GLC, and its infrared spectrum and retention times agreed with those of 1,8-cineole. This fraction formed the resorcinol adduct, m.p. 80–85° C (17), in fair yield. Peak 2 was not obtained pure in sufficient amount to allow positive identification. Its infrared spectrum resembled that of 1,8-cineole.

Peak 6 was also obtained only impure. However, its retention times and the ultraviolet spectrum were similar to those of *p*-cymene. Since only the other two oxides are the impurities present, there is little doubt that peak 6 corresponds to *p*-cymene.

*Camphene (Peak No. 1)*

The retention times of peak 1 on different columns agreed with those of camphene.  $\alpha$ -Terpineol (40 g) was dissolved in 90% ethanol (160 ml) containing sulphuric acid (40 ml) and the mixture was refluxed for 1 hour. The steam-volatile terpenes (22 g) were recovered as before and fractionally distilled. The first fraction, b.p. 64–68° C at 20 mm pressure, contained about 80% of peak 1 and crystallized on seeding with camphene. The crystals were filtered off and recrystallized from ethanol–water, m.p. 47.5–49° C, undepressed in admixture with synthetic camphene.

*Peak No. 8*

This fraction was obtained only in very small amounts which were insufficient for characterization. Its spectral properties were similar to those of  $\Delta^{2,8(9)}$ -*p*-menthadiene (7).

## RESULTS AND DISCUSSION

The amount of unreacted  $\alpha$ -terpineol (I) and the percentage yield of the products formed in the reaction with aqueous oxalic acid after reaction times of 1/2 to 12 hours are shown in Figs. 1(a) and 1(b). Maximum yields of terpinolene (II), 1,8-cineole (VI), and oxide 1 were obtained within 1 to 3 hours and then diminished rapidly (Fig. 1(a)). The maximum yield of dipentene (III) was reached very quickly, decreasing only slowly after 4 to 6 hours.  $\alpha$ -Terpinene (IV),  $\gamma$ -terpinene (V),  $\Delta^{2,4(8)}$ -*p*-menthadiene (VII), *p*-cymene, and peak 8 reached their maximum concentrations only after 8 hours, all but VII decreasing from then on. When pure II was treated under the same conditions for 6 hours, only IV, V, VII, and peak 8 were obtained (in approximately the same ratio); less than 1% of III was recorded. Thus, the four *p*-menthadienes, IV, V, VII, and peak 8, are clearly isomerization products of terpinolene. Pure limonene, under the same conditions, did not yield any isomerization or hydration products but resinified somewhat, explaining the loss of III as the reaction proceeds. Under similar conditions 1,8-cineole (VI) gave a product having the same chromatographic spectrum as was obtained for the reaction product obtained from  $\alpha$ -terpineol (I) itself, 2–3% of I also being recorded. It

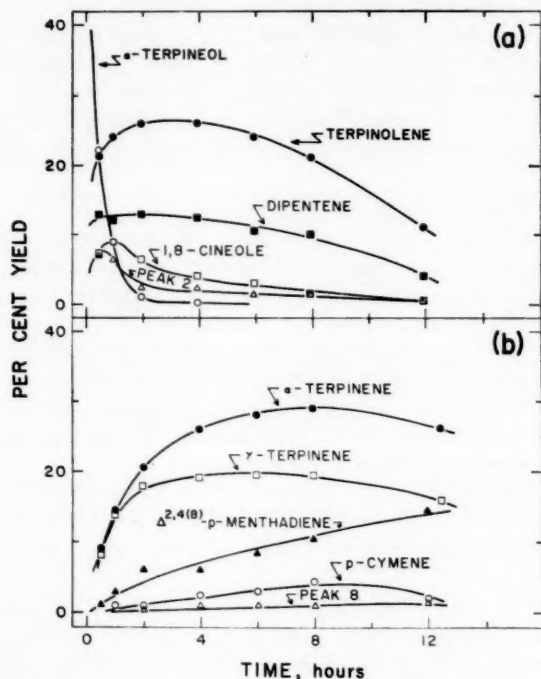


FIG. 1. Yields of individual components in the reaction of  $\alpha$ -terpineol with aqueous oxalic acid: (a) initial products, (b) isomerization products.

can be concluded, therefore, that VI and I are in equilibrium with one another under these conditions. The similarity of the shape of the curves obtained for oxide 1 (peak 2) and VI (Fig. 1(a)) suggests that oxide 1 is formed in a similar reversible reaction. This could only be possible if this oxide is 2,8-cineole (dihydropinol), a finding which is further strengthened by the fact that its retention time is in good agreement with that expected for dihydropinol (as deduced from boiling points).

Thus, the reaction of  $\alpha$ -terpineol with aqueous oxalic acid appears to proceed as follows:

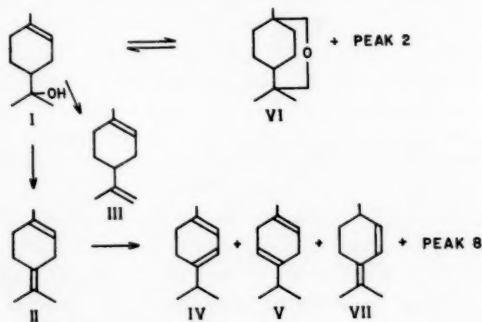


FIG. 2.



Semmler (20) has shown that alcoholic sulphuric acid isomerizes  $\alpha$ -terpinene (IV) to V and II. Thus it is possible that these *p*-menthadienes are in a state of equilibrium under acid conditions. The above findings clearly show why it has been impossible to obtain II, IV, and V in a pure state when prepared under acidic reaction conditions.

The preferential formation of terpinolene (maximum yield about twice that of dipentene) is contrary to what would be expected from the postulate put forward by Brown *et al.* (21), according to which the exo-double bond should be formed in smaller amounts than the isopropenyl derivative. These authors quote Flawitzky (3) as having obtained limonene from I by dehydration with alcoholic sulphuric acid and use this as further evidence that tertiary alcohols of this type resist formation of an exo-double bond. Actually, Flawitzky used the alcoholic sulphuric acid to hydrate  $\alpha$ -pinene (turpentine) to give I and the latter was then heated in a sealed tube with excess acetic anhydride to give appreciable amounts of limonene besides  $\alpha$ -terpinyl acetate. As will be shown below, this reaction appears to be a deacetoxylation rather than a dehydration and proceeds via a different mechanism. Moreover, Brown *et al.* do not refer to the much more comprehensive studies of Wallach (1, 2), which clearly show that the exo-double bond, as in II, may be formed in substantial amounts in the acid-catalyzed dehydration. It is thus doubtful whether the olefin formation from compounds of the  $\alpha$ -terpineol type can be included in the generalization put forward by Brown *et al.* Also, the isomerization of terpinolene does not proceed entirely according to this postulate, the exo-isomer VII being a major product besides the two endo-isomers IV and V. In a later communication, Brown (22) points out that their postulate has been misinterpreted by some workers by not considering the stability of the double bonds in cyclohexanes in conjunction with the corresponding cyclopentane derivatives. However, in the first paper, Brown *et al.* discuss the dehydration of  $\alpha$ -terpineol and related compounds without any reference to the corresponding cyclopentanol. Recently (23), it has been shown that the whole question of the relative stabilities of methylene cycloalkanes and 1-methyl cycloalkenes is subject to some controversy.

In view of the above discrepancies, the work of Wallach and Flawitzky was repeated and the reaction with other acidic dehydrating agents was also investigated. The steam-volatile reaction products were analyzed by GLC as before and the results obtained are summarized in Table II. In the reaction with aqueous sulphuric and phosphoric acids, the reaction products had the same qualitative chromatographic spectra as that obtained with aqueous oxalic acid, confirming in essence Wallach's findings. When  $\alpha$ -terpineol was dissolved in twice its volume of acetone and added dropwise to boiling aqueous sulphuric acid through which steam was passed (24), the steam-volatile product differed little from that obtained in the short-time reaction with aqueous oxalic acid, except that oxide 1 was produced in somewhat larger amounts and two additional peaks (11 and 13) became more prominent. Treatment with 90% ethanol-sulphuric acid (4:1 v/v) also gave a product of similar composition containing, however, a new major compound (peak 1) identified as camphene. Fused anhydrous potassium hydrogen sulphate also gave results similar to those obtained with aqueous oxalic acid, oxide formation being somewhat suppressed. This is contrary to the results Wallach obtained with "sharply dried" potassium hydrogen sulphate (2). Therefore, hydrogen sulphate was fused until fuming became extensive (pyrosulphate formation), and this was used in excess. Under these conditions I reacted to give a high yield of the oxides and camphene, but only traces of III. Thus, Wallach's findings could not be confirmed in this instance. That water is not responsible for any difference in the reaction follows from the results obtained with

phthalic anhydride. Here, anhydrous conditions again give a mixture similar to that obtained with aqueous acids.

The dehydration of  $\alpha$ -terpineol with 50% aqueous acetic acid proceeds slowly (see Table II) and allows a better study of the early stages of the reaction. II and III are distinctly the first dehydration products and the yield of the former increases much faster than that of the latter as the reaction proceeds. Oxide formation and isomerization of II is slow, making the reaction well suited for the preparation of II and III, especially so since these two *p*-menthadienes can be separated by fractional distillation. The different results obtained with glacial acetic acid (or acetic anhydride) are noteworthy (see below).

Mosher (25) proposed for the acid-catalyzed isomerization of  $\alpha$ -pinene (X) to the *p*-menthadienes rearrangement to the intermediate carbonium ion XI. Loss of a proton leads to terpinolene (II) and dipentene (III), and (via the carbonium ion XII) to  $\alpha$ -terpinene (IV) and  $\gamma$ -terpinene (V) (Fig. 3). This mixture of *p*-menthadienes is very

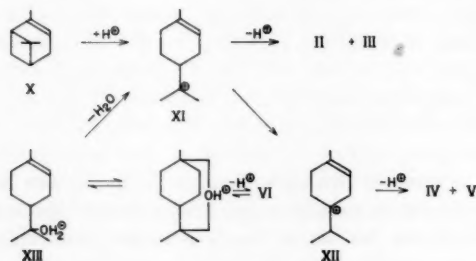


FIG. 3.

similar to that obtained in the acid-catalyzed dehydration of  $\alpha$ -terpineol. Thus, it is likely that  $\alpha$ -terpineol, in the protonated form (XIII), loses the elements of water to give the same intermediate carbonium ion XI. The present findings that terpinolene isomerizes readily to IV, V, and VII, but not to III, suggest that the ion XI rearranges rapidly and irreversibly to ion XII. The formation of VII, however, demands the presence of another intermediate ion. Cyclization of the protonated alcohol (XIII) and loss of a proton would lead to 1,8-cineole (VI) in a reversible reaction.

Refluxing I with excess acetic anhydride for 16 hours gave a yield of 50%  $\alpha$ -terpinyl acetate, 32% III, and small amounts of *p*-menthadienes and oxides (see Table II), confirming, in essence, the findings of Flawitzky (3). The reaction with glacial acetic acid is similar, though the amount of  $\alpha$ -terpineol which had reacted after 12 hours was only 30%. Since, in this reaction, I may be converted to the acetate first and this, on loss of the elements of acetic acid, could give III as the main elimination product,  $\alpha$ -terpinyl acetate was treated in the same manner. Appreciable amounts of III, and smaller amounts of the other *p*-menthadienes, were formed (see Table III). Thus, it is possible that the preferential formation of III is due to deacetoxylation of the acetate rather than the dehydration of the parent alcohol.

Recently, Roček (26) has studied the kinetics of the dehydration of 1-methyl cyclohexanol as well as the deacetoxylation of the derived acetate, using acetic acid containing small amounts of sulphuric acid at room temperature. From the data obtained Roček concluded that both the dehydration and the deacetoxylation proceeds via the same intermediate carbonium ion and the rate-controlling step is given as the elimination of

water from the protonated alcohol, or of acetic acid from the protonated ester. In the reaction of  $\alpha$ -terpineol and its acetate with this reagent at room temperature or under reflux, appreciable amounts of camphene and the oxides, but only small amounts of the *p*-menthadienes, were obtained (see Tables II and III). The yield of steam-volatile products dropped markedly and a new peak (No. 15) in the  $\alpha$ -terpineol range was recorded. Thus, with this reagent a third type of reaction was encountered in which the normal dehydration (or deacetoxylation) products did not survive the reaction, if these were formed at all. Similar results were also obtained when formic acid was used as dehydrating agent (Table II). Since this was no longer a normal dehydration reaction, it was not further investigated.

The presence of small amounts of *p*-cymene (peak No. 6) in most reaction products deserves some comment. Its formation in the acid-catalyzed dehydration of  $\alpha$ -terpineol was already suspected by Wallach and Kerkhoff (2). Since the reaction conditions are not conducive to dehydrogenation, disproportionation of one or more of the *p*-menthadienes to *p*-cymene and *p*-menthenes may take place. This would account for the presence of the trace components in the *p*-menthene range.

#### CONCLUSIONS

The dehydration of  $\alpha$ -terpineol with acidic reagents can occur in two different ways: (a) With aqueous acids, anhydrous potassium hydrogen sulphate, or phthalic anhydride, terpinolene is the major reaction product in the early stages of the reaction. About half as much dipentene and smaller amounts of 1,8-cineole and a second oxide, possibly 2,8-cineole, are also formed. As the reaction proceeds, terpinolene isomerizes to give mainly  $\alpha$ -terpinene, somewhat less  $\gamma$ -terpinene and  $\Delta^{2,4(8)}$ -*p*-menthadiene, and a small amount of an unidentified terpene. Drastic conditions, or long reaction times, tend to cause resinification. The oxides are in equilibrium with  $\alpha$ -terpineol and give the same reaction products on prolonged treatment. (b) With acetate-forming reagents, dipentene is formed preferentially. Apparently the acetate is an intermediate and subsequent loss of the elements of acetic acid favors the production of this *p*-menthadiene.

The present findings show that by proper choice of conditions the preferential formation of terpinolene, dipentene,  $\alpha$ - and  $\gamma$ -terpinene, or  $\Delta^{2,4(8)}$ -*p*-menthadiene can be achieved. However, it is impossible to synthesize by this means any one of these *p*-menthadienes without concomitant formation of smaller amounts of several isomers. Only in very favorable instances can such mixtures be separated completely by fractional distillation. If very pure specimens of these *p*-menthadienes are required other sources must be sought, or the products obtained in the above reactions can be fractionated on a 0.01- to 0.1-g scale by preparative gas-liquid chromatography.

#### ACKNOWLEDGMENTS

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# HYDROGEN ATOM ABSTRACTION BY ETHYL- $d_5$ RADICALS. PART II<sup>1</sup>

P. J. BODDY<sup>2</sup> AND E. W. R. STEACIE

## ABSTRACT

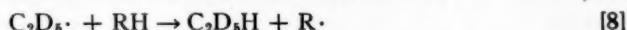
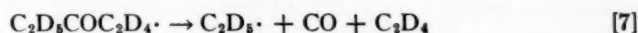
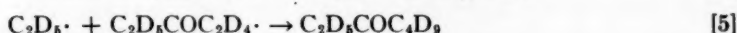
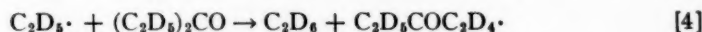
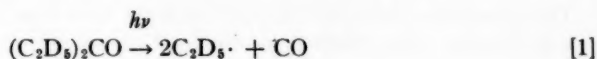
Further experiments are reported on the hydrogen atom abstraction reactions of deuterated ethyl radicals produced by the photolysis of 3-pentanone- $d_{10}$ .

The compounds studied include hydrogen, *n*-hexane, and cyclohexane. The activation energies for hydrogen atom abstraction relative to ethyl- $d_5$  recombination are respectively  $11.3 \pm 0.5$ ,  $10.1 \pm 0.5$ , and  $10.4 \pm 0.5$  kcal/mole.

## INTRODUCTION

Recently experimental data were reported for hydrogen atom abstraction from a series of typical alkanes by ethyl- $d_5$  radicals (1). This paper represents a continuation of that work in an effort to provide further points of comparison with the much investigated methyl radical reactions (2). The apparently arbitrary choice of compounds was dictated largely by what was possible analytically by conventional distillation and mass spectrometric techniques.

The photolysis of diethyl ketone is understood in some detail (3, 4). The mechanism is assumed to be similar for the deuterated species and is as follows (rate constants, of course, may be different):



It can be shown that

$$\frac{k_8}{k_2^{1/2}} = \frac{R_{C_2D_5H}}{R_{C_4D_{10}}^{1/2}[RH]}$$

and

$$\frac{k_8}{k_4} = \frac{[\text{ketone}]}{[RH]} \cdot \frac{R_{C_2D_5H}}{R_{C_2D_6}}$$

where  $R_{C_2D_5H}$  and  $R_{C_2D_6}$  are the rates of formation of ethane- $d_5$  and ethane- $d_6$  from reactions [8] and [4]. Hence, the activation energy and frequency factor of reaction [8] may be determined relative to reactions [2] or [4] both of which are quantitatively understood (5, 1, 6, 7).

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Difficulty arises due to the fact that the diethyl ketone is not completely deuterated. The sample used by us contained only a small percentage of the  $d_8$ -ketone, and the necessary corrections to the data, which have previously been described in detail (1), were made accordingly.

Another complication is due to the occurrence of reaction [7], which becomes considerable above 200° C. This may lead to errors in the estimation of  $C_2D_6$  from reaction [4] since it is assumed that all of the  $C_2D_4$  arises from reaction [3] and that this is equal to the  $C_2D_6$  from the same source. In the absence of quantitative knowledge of reaction [7], it is difficult to estimate the magnitude of the error involved. In the present work only the hydrogen experiments extended much above this temperature and since the data gave a linear Arrhenius plot throughout the whole range, it is concluded that the error is not large in this case.

Some experiments were attempted with methane and benzene. With these compounds, as in the corresponding methyl radical reactions (2), the rate constants for hydrogen atom abstraction appear to be relatively small. This necessitates working at high RH: ketone ratios and elevated temperatures. Under these conditions reaction [7] becomes much more significant and the experiments were unsuccessful.

#### EXPERIMENTAL

The apparatus and experimental methods have been described previously (1).

*n*-Butane- $d_{10}$  was collected as the fraction between -165° C and -125° C and its identity was checked by mass spectrometry. A correction was made for the *n*-butane- $d_9$  content which was found to be a constant fraction.

#### MATERIALS

The purity of the 3-pentanone- $d_{10}$  was discussed previously (1).

*n*-Hexane and cyclohexane were Phillips Research Grade materials. They were degassed and stored under vacuum in blackened bulbs behind mercury cutoffs. Purities were in excess of 99.5%.

Hydrogen was purified before each experiment by passage through a heated palladium thimble.

#### RESULTS

The experimental data for the three compounds are presented in Tables I-III. The calculated values of  $\log_{10}(k_3/k_4)$  are plotted in Fig. 1 as a function of  $1/T$ . The familiar departure from linearity at low temperatures (1, 4, 7) is apparent. The slopes and intercepts were calculated by the least squares method. Points lying on the dashed portion of the curves (lowest temperatures) were not included in the analysis. The results are summarized below. The values for  $E_4 - \frac{1}{2}E_2$  and  $\log_{10}(A_4/A_2^{1/2})$  were determined previously (1) (the units throughout are molecules/ml, and seconds):

$$E_4 - \frac{1}{2}E_2 = 9.0 \pm 0.5 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_4}{A_2^{1/2}} = 8.36 \pm 0.20.$$

TABLE I  
Ethyl- $d_5$  with hydrogen

Ketone	Hydrogen	Temp.,	Time,	$R_{C_2D_6H}$	$R_{C_2D_6}$	$R_{C_2D_4}$	$R_{C_2D_3H}$	$R_{C_4D_{10}}$	$2 + \log \frac{k_3}{k_4}$	$13 + \log \frac{k_4}{k_3^{\frac{1}{2}}}$	$15 + \log \frac{k_4}{k_3^{\frac{1}{2}}}$
molecules/ml $\times 10^{-17}$	$\times 10^{-17}$	$^{\circ}K$	sec	molecules/ml sec $\times 10^{-12}$							
9.66	8.89	375	3600	0.108	0.906	0.528	0.020	5.30	1.25	0.24	1.51
13.02	8.23	391	4740	0.132	1.29	0.600	0.071	6.24	1.27	0.29	1.55
7.23	7.23	501	3660	1.78	4.05			3.37	1.64	1.45	3.09
5.42	5.82	481	2760	1.18	3.10	0.105	0.0216	3.61	1.55	1.42	2.97
4.83	5.25	469.5	3600	0.772	2.21	0.145	0.019	3.76	1.53	1.29	2.82
12.72	5.07	448	3180	0.732	4.77	0.510	0.0595	7.70	1.51	1.05	2.56
7.48	6.92	432.5	3840	0.524	2.27	0.423	0.0313	6.03	1.45	0.92	2.37
4.15	3.92	419	4740	0.0929	0.556	0.139	0.0171	2.51	1.24	1.80	2.05
8.38	9.36	392	3600	0.186	1.32	0.649	0.0328	7.95	1.33	0.35	1.98
7.19	6.33	374	3780	0.089	1.12	0.694	0.030	6.58	0.98	0.41	1.40
6.33	5.15	356	3600	0.0543	1.05	0.736	0.0348	6.72	0.51	0.14	0.82
5.76	3.84	553	3655	4.40	12.6	1.01	0.224	2.16	1.70	2.12	3.81
5.06	9.19	515	3600	2.39	7.62	0.218	0.115	2.05	1.62	1.95	3.57
			4640	2.59	3.94	0.096	0.0553	3.03	1.56	1.61	3.18

TABLE II  
Ethyl- $d_5$  with  $n$ -hexane

Ketone	$n$ -Hexane	Temp., °K	Time, sec	$R_{C_2D_5H}$	$R_{C_2D_6}$	$R_{C_2D_4}$	$R_{C_2D_3H}$	$R_{C_4D_{10}}$	$1 + \log \frac{k_1}{k_2}$	$13 + \log \frac{k_1}{k_2}$	$14 + \log \frac{k_1}{k_2}$
molecules/ml $\times 10^{-17}$						molecules/ml sec $\times 10^{-12}$					
3.11	4.89	497.5	3600	1.66	2.05	0.185	0.0034	2.53	0.73	1.58	2.31
3.77	4.32	525	3640	2.77	4.07	0.070	0.056	3.91	0.74	1.72	2.48
4.63	4.51	467	3816	1.07	2.35	0.379	0.044	4.73	0.70	1.28	1.99
3.89	4.82	447	4500	0.594	1.20	0.344	0.0042	3.82	0.70	1.06	1.76
4.60	4.31	428	5540	0.367	1.13	0.421	0.015	4.90	0.67	0.847	1.53
4.37	6.14	404	4330	0.261	0.814	0.433	0.017	3.69	0.62	0.660	1.28
5.12	6.44	388.3	3825	0.186	0.825	0.497	0.017	4.37	0.55	0.393	1.05
5.23	5.77	360	3665	0.073	0.616	0.475	0.017	5.22	0.45	0.039	0.518

TABLE III  
Ethyl- $d_5$  with cyclohexane

Ketone	Cyclohexane	Temp., °K	Time, sec	$R_{C_2D_5H}$	$R_{C_2D_6}$	$R_{C_2D_4}$	$R_{C_2D_3H}$	$R_{C_4D_{10}}$	$1 + \log \frac{k_1}{k_2}$	$13 + \log \frac{k_1}{k_2}$	$14 + \log \frac{k_1}{k_2}$
molecules/ml $\times 10^{-17}$						molecules/ml sec $\times 10^{-12}$					
4.36	4.32	521	3635	2.86	3.70	0.375	—	1.89	0.91	1.75	2.66
5.29	2.99	484	4040	1.22	2.94	0.426	0.022	2.72	0.88	1.46	2.34
6.11	8.39	403	3640	0.588	1.41	0.725	0.012	6.10	0.73	0.67	1.40
7.60	7.47	380	4000	0.225	1.12	0.703	—	7.51	0.60	0.33	0.93
10.0	13.6	371.5	3670	0.126	0.292	0.113	0.007	1.16	0.67	0.21	0.89
8.80	21.6	395	3600	0.334	0.342	0.093	0.005	0.954	0.72	0.46	1.18
6.55	14.7	450	3600	0.701	0.563	0.028	0.002	0.399	0.75	1.11	1.86
5.26	11.5	496	3600	0.946	0.650	0.001	0.005	0.131	0.81	1.53	2.34
5.67	12.8	477	4100	0.874	0.647	—	—	0.192	0.76	1.42	2.18
5.90	11.7	566	7933	1.53	0.975	0.079	0.025	0.044	0.90	1.88	2.78

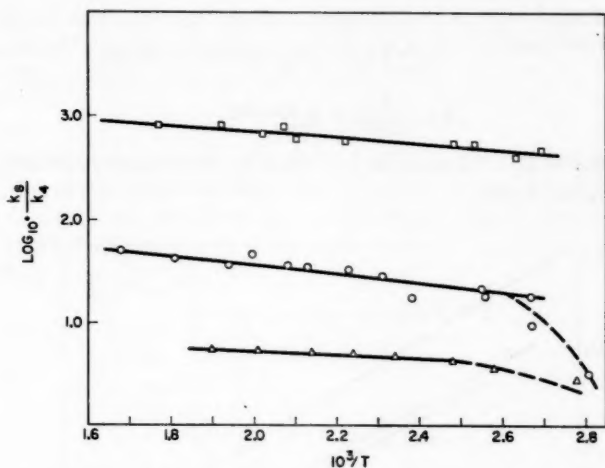


FIG. 1.  $\text{Log}_{10}(k_8/k_4)$  as a function of  $1/T$ . Curves displaced up by number of units in parentheses.  $\circ$   $\text{H}_2$  (+2),  $\triangle$   $n\text{-C}_6\text{H}_{14}$  (+1),  $\square$   $\text{cyclo-C}_6\text{H}_{12}$  (+3).

For hydrogen

$$E_{8a} - E_4 = 2.3 \pm 0.2 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{8a}}{A_4} = 0.56 \pm 0.086;$$

whence

$$E_{8a} - \frac{1}{2}E_2 = 11.3 \pm 0.5 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{8a}}{A_2^{1/2}} = 8.92 \pm 0.2.$$

For *n*-hexane

$$E_{8b} - E_4 = 1.06 \pm 0.1 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{8b}}{A_4} = 0.19 \pm 0.055;$$

therefore

$$E_{8b} - \frac{1}{2}E_2 = 10.1 \pm 0.5 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{8b}}{A_2^{1/2}} = 8.55 \pm 0.2.$$

For cyclohexane

$$E_{8c} - E_4 = 1.4 \pm 0.14 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{8c}}{A_4} = 0.47 \pm 0.07;$$

therefore

$$E_{sc} - \frac{1}{2}E_2 = 10.4 \pm 0.5 \text{ kcal/mole,}$$

$$\log_{10} \frac{A_{sc}}{A_2^{1/2}} = 8.83 \pm 0.2.$$

Plots of  $\log_{10}(k_s/k_2^{1/2})$  as a function of  $1/T$  (Fig. 2) yield results agreeing with those above within the quoted error.

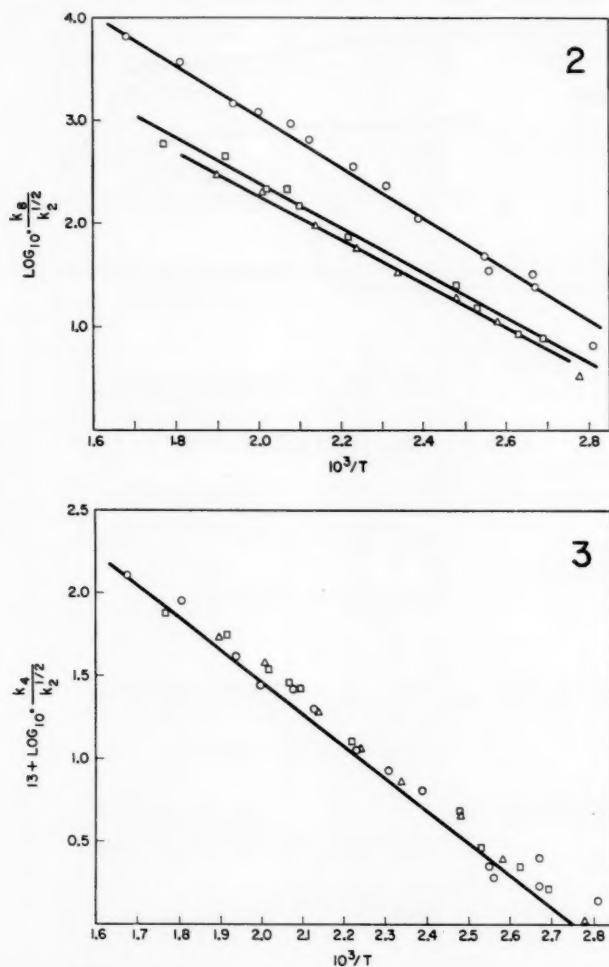


FIG. 2.  $\log_{10}(k_s/k_2^{1/2})$  as a function of  $1/T$ . Key as in Fig. 1. Hydrogen curve displaced up by 2 units.

FIG. 3.  $\log_{10}(k_4/k_2^{1/2})$  as a function of  $1/T$ . Key as in Fig. 1.

In Fig. 3 the data for abstraction from the ketone during these experiments are plotted. The solid line is the result of experiments on the ketone alone (1). There is a tendency



for the points to lie above the line by about 15% in  $k_4/k_2^{1/2}$ , but the slopes are not in disagreement and it appears there are no serious errors involved either in the chemical analyses or the methods used to compute the data.

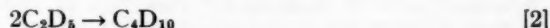
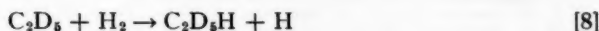
## DISCUSSION

The reaction between ethyl- $d_0$  radicals and molecular deuterium has been studied (8) and it was tentatively suggested that the activation energy for abstraction of a hydrogen atom from molecular hydrogen was  $11.5 \pm 1$  kcal/mole, in very good agreement with the value reported above.

If we write



and



$k_{8a}/k_{2a}^{1/2}$  may be calculated to be  $1.0 \times 10^{-13}$  at  $182^\circ\text{C}$  (4, 7).  $k_8/k_2^{1/2}$  is  $3.4 \times 10^{-13}$  at the same temperature.

The ratio of these figures is quite close to that for the corresponding methyl radical reactions ( $\text{CD}_3 + \text{H}_2$ ,  $\text{CH}_3 + \text{D}_2$ ), which is 5.3 (9). The ratio is even closer to that for the reactions

$$\frac{\text{CH}_3 + \text{H}_2}{\text{CH}_3 + \text{D}_2} = 3.6 \quad \text{at } 182^\circ\text{C} \quad [9]$$

$$\frac{\text{CD}_3 + \text{H}_2}{\text{CD}_3 + \text{D}_2} = 3.7$$

and suggests that possibly ethyl- $d_0$  and ethyl- $d_5$  are more similar than the corresponding pair methyl- $d_0$  and methyl- $d_3$ .

It is interesting to observe that, as compared with methyl, ethyl radicals seem to react relatively faster with hydrogen than with hydrocarbons at  $182^\circ\text{C}$ . Some rate constants (expressed in the same way as above) are:

$\text{CH}_3 + \text{H}_2$	$12.6 \times 10^{-13}$ (9)	$\text{C}_2\text{D}_5 + \text{H}_2$	$4.3 \times 10^{-13}$
+ neo- $\text{C}_5\text{H}_{12}$	6.3 (2)	+ neo- $\text{C}_5\text{H}_{12}$	0.45 (1)
+ iso- $\text{C}_4\text{H}_{10}$	42 (2)	+ iso- $\text{C}_4\text{H}_{10}$	6.1 (1)

The reason for this is not understood.

The rate constant  $(k_8/k_2^{1/2})_{182^\circ\text{C}}$  for *n*-hexane is  $5.7 \times 10^{-13}$  (ml/molecule sec) $^{1/2}$ . Correcting for the presence of the six primary hydrogen atoms (2) using the neopentane data (1), the rate constant per secondary hydrogen atom becomes  $0.68 \times 10^{-13}$ , in excellent agreement with the figure  $0.70 \times 10^{-13}$  obtained for *n*-butane (1). This may be compared with the figure for the reaction of ethyl- $d_0$  radicals with *n*-heptane (10), where  $(k_8/k_2^{1/2})_{182^\circ\text{C}}$  (our notation) is  $10.7 \times 10^{-13}$ ; after correcting for the primary hydrogens using the ethyl- $d_5$  data, which should be approximately correct (the correction is very small in any case), the rate constant per secondary hydrogen atom becomes  $1.05 \times 10^{-13}$ . Thus, it appears that ethyl- $d_0$  is about 50% more reactive than ethyl- $d_5$ . It is rather perplexing

that an effect similar in magnitude but in the opposite direction is observed for the reaction of methyl- $d_0$  and  $-d_3$  with  $H_2$  and  $D_2$  (9). A difference has been observed in the reaction of methyl radicals ( $-d_3$  and  $-d_0$ ) with neopentane amounting to about 15% and in the same direction that we observe, i.e., methyl- $d_0$  more reactive (11).

The rate constant for cyclohexane at  $182^\circ C$  is  $7.2 \times 10^{-13}$  (ml/molecule sec) $^{1/2}$  corresponding to a value of  $0.6 \times 10^{-13}$  per hydrogen atom. This agrees with the methyl radical results where cyclohexane was found to give a value typical of a secondary paraffinic hydrogen atom (2).

The authors wish to thank Mrs. R. H. Riem, who carried out the mass spectrometric analyses.

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## DEUTERATED ORGANIC COMPOUNDS

### XXII. SYNTHESIS OF SOME DEUTERATED BENZENE DERIVATIVES<sup>1</sup>

R. N. RENAUD, D. KOVACHIC,<sup>2</sup> AND L. C. LEITCH

#### ABSTRACT

The deamination of certain aromatic amines in deuteriohypophosphorous acid with sodium or isoamyl nitrite has been used to label aromatic compounds in a specific position with deuterium. Aniline 2,3-*d*<sub>2</sub> was synthesized by this method.

Exchange with deuterium sulphate has been extended to the deuteration of nitrotoluenes, bromotoluenes, and polychlorobenzenes.

Previous communications in this series (1, 2, 3) have dealt very largely with the synthesis of deuterated aliphatic compounds. Aromatic compounds were investigated only incidentally and then interest was centered on introducing deuterium into the side chain rather than into the nucleus. In this paper the deuteration of aromatic compounds will be formally discussed.

The total replacement of hydrogen by deuterium in the aromatic series is in general effected more readily than in aliphatic compounds. Some years ago one of us (4) showed that benzene-*d*<sub>6</sub> could be conveniently prepared by exchange with deuterium oxide at 100° C. in the presence of platinum black. Others (5, 6, 7) have since reported that benzene derivatives such as benzoic acid or aniline and polynuclear hydrocarbons can be deuterated as well. In contrast, alkanes undergo exchange under these conditions only when deuterium gas is also present.

The exchange with deuterium oxide catalyzed by platinum black yields compounds completely deuterated in the ring. The method is therefore inapplicable for the preparation of compounds containing deuterium in specific positions. Several methods of obtaining such compounds have, however, been investigated in the past.

In early attempts to prepare deuterated benzenes, calcium salts of aromatic acids were decarboxylated in the presence of calcium deuterioxide. Morita and Titani (8) prepared benzene-*d*<sub>1</sub> by this method from anhydrous calcium benzoate. Later, Redlich and Stricks (9) obtained benzene-1,2-*d*<sub>2</sub> from calcium phthalate and Weldon and Wilson (10) synthesized benzene-1,3,5-*d*<sub>3</sub> from the calcium salt of mesitylene carboxylic acid. Finally, Erlenmeyer carried the method to its logical conclusion by preparing benzene-*d*<sub>6</sub> from calcium mellitate (11). The reaction was later reinvestigated by Best and Wilson (12), who showed that the isotopic purity of the products was low due to exchange under the drastic conditions employed.

Another method of obtaining deuterated benzenes is the hydrolysis of Grignard reagents with deuterium oxide or deuterium chloride. However, only one atom of deuterium can usually be introduced in this way. Redlich and Stricks (13) had prepared benzene-1,2-*d*<sub>2</sub> from 1,2-diiodobenzene in this manner but later work by Best and Wilson (12) showed the dimagnesium reagent from 1,4-dibromobenzene exchanged with ether presumably by a free radical mechanism to give benzene-1,4-*d*<sub>2</sub> of low isotopic purity. They circumvented this difficulty by introducing the deuterium in two stages, i.e. by two separate Grignard preparations and hydrolyses. In any event the application of Grignard

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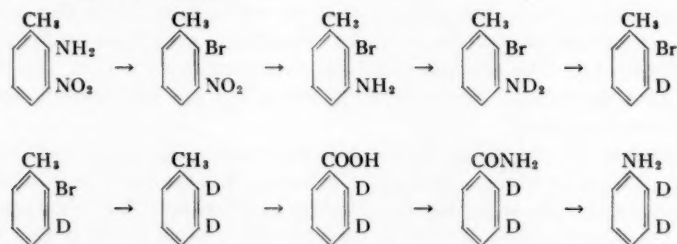
<sup>2</sup>Terminated May, 1959.

reagents to the problem of deuteration is severely restricted by the incompatibility of organometallic halides with several other functional groups such as nitro, carboxyl, amino, etc. Nevertheless, the Grignard synthesis is probably the best method of preparing benzene- $d_1$ , the three deuterated toluenes, and perhaps other deuterated alkyl benzenes.

Deamination is a well-known method of replacing an amino group by hydrogen (14). It is usually carried out by heating the diazonium salt of the amine in ethanol. The mechanism of this reaction has recently been shown by deTar and Turetzky (15) to be a free radical process. It is not attractive for replacing an amino group by deuterium because ethyl alcohol labelled with deuterium on the methylene group is required. In the present work deamination in isopropyl alcohol was investigated since isopropyl-2- $d$  alcohol,  $\text{CH}_3\text{CD}(\text{OH})\text{CH}_3$ , is easily prepared from acetone and lithium aluminum deuteride. However, the yields obtained in the decomposition of the diazonium fluoborate in isopropyl alcohol were very poor and the method was abandoned in favor of deamination in hypophosphorous acid.

In conventional deamination with hypophosphorous acid (16) the amine is first diazotized in hydrochloric or sulphuric acid and the solution of the diazonium salt is treated with an excess of 50% hypophosphorous acid. Since preparation of diazonium salts in deuterium oxide as solvent is prohibitive on economic grounds, it was decided to deaminate some representative amines directly in 50% hypophosphorous acid solutions by addition of sodium nitrite. It was felt hypophosphorous acid would be strong enough to allow diazotization to take place. This was indeed found to be the case. Bromobenzene was obtained in 70% yield from 2-bromoaniline. A search of the literature revealed only one case of diazotization in  $\text{H}_3\text{PO}_2$ , Henry and Finnegan (17) having deaminated 5-aminotetrazole in 5% hypophosphorous acid. In the present work 2-bromo-3-methylaniline, 1-naphthylamine, and pentachloroaniline were similarly deaminated in 50% hypophosphorous acid.

The replacement of  $\text{NH}_2$  by deuterium by the above method was an important step in a synthesis of aniline-2,3- $d_2$  which was required in connection with some work in N.M.R. spectroscopy (18). The most feasible route to this compound appeared to be the sequence of reactions shown below:



The preparation of the starting compound, 3-nitro-2-aminotoluene, has been reported in *Organic syntheses* (19). The amino group was replaced by bromine by a Sandmeyer reaction. The nitro group was successfully reduced to amino without simultaneous loss of bromine by reduction with activated iron powder in dioxane as described by Hazlett and Dornfeld (20). Deamination in hypophosphorous acid containing a low concentration of deuterium has been shown to be subject to a high deuterium isotope effect in favor of hydrogen (21). This meant that rigorous exclusion of exchangeable hydrogen was absolutely

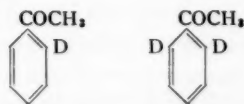
necessary to obtain a high concentration of deuterium in the product. Consequently, hypophosphorous acid was exchanged with deuterium oxide as described by Hammond and Grundemeier (22) until the hydrogen atom signal in the N.M.R. spectrum was absent. Similarly the hydrogen in the amino group of the amine was replaced by deuterium by several exchanges in slightly alkaline deuterium oxide. The 2-bromotoluene-3*d* isolated in 50% yield was 96 mole%  $C_7H_6BrD$ . The second deuterium atom was introduced via a Grignard synthesis. The deuterium content of the toluene-2,3-*d*<sub>2</sub> was 83 mole %. It was oxidized to benzoic-2,3-*d*<sub>2</sub> acid in aqueous alkaline permanganate without loss of deuterium. Aniline-2,3-*d*<sub>2</sub> was obtained from the acid via the acid chloride and the amide by the Hofmann degradation.

The benzene-1,2-*d*<sub>2</sub> prepared from the deuterated aniline by deamination analyzed 82.1%  $C_6H_4D_2$  and 17.1%  $C_6H_6D$ . The slightly low content of deuterium may be due to a small loss of deuterium by exchange in each of the two reactions involving introduction of deuterium. In any event the compound was pure enough isotopically for the purpose. Deamination by means of deuteriohypophosphorous acid thus offers a convenient means of replacing an amino group by deuterium in an aromatic compound. Another recent example of its use is the deamination of vicinal xylidine to 1,3-xylene-2-*d* by Fraser (23).

Yet another method of deuterating aromatic compounds is the action of deuterium chloride in the presence of anhydrous aluminum chloride. Klit and Langseth prepared benzene-*d*<sub>6</sub> by this method (24). The reaction is essentially an exchange catalyzed by the Lewis acid  $AlCl_3$ . It probably cannot be used for deuterating in a specific position.

Important confirmation of an earlier prediction by Ingold, Raison, and Wilson (25) was obtained in 1936 when these authors observed a reasonably rapid exchange between benzene and 50 mole % deuterium sulphate in deuterium oxide at room temperature without any appreciable sulphonation. Several years later in continuation of their brilliant work on the spectroscopic investigation of the structure of benzene, Ingold, Wilson, and co-workers turned again to the exchange method to prepare benzene-*d*<sub>6</sub> and 1,4-dibromobenzene-*d*<sub>4</sub> (12). In deuterating bromobenzene by this method they were unable to avoid undue sulphonation. Apparently in this case the rates of sulphonation and exchange are very similar. A third deuterobenzene, the 1,3,5-*d*<sub>3</sub> isomer was prepared from aniline, in which exchange occurs under comparatively milder conditions than in benzene. It is sufficient to heat the hydrochloride in deuterium oxide for a day to establish equilibrium. Deuterium enters the ortho and para positions. After several such exchanges the deuterium in the amino group was washed out with ordinary water and the amine was deaminated to benzene-1,3,5-*d*<sub>3</sub>. Since the paper by Best and Wilson (12) no appreciable use has been made of this reaction to deuterate aromatic compounds.

One of the aims of the present work was to extend the exchange method to a variety of substituted benzenes in order to obtain compounds of interest for infrared measurements. Two of these were acetophenone-2-*d* and acetophenone-2,6-*d*<sub>2</sub>. The synthesis of 2-deuteroacetophenone was straightforward. It started with 2-bromotoluene, which was

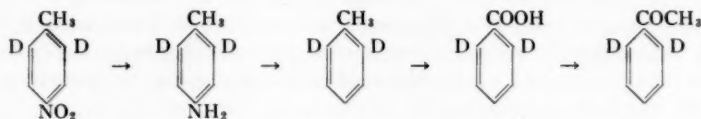


converted to toluene-2-*d* by the Grignard reaction discussed above. The toluene-2-*d* was oxidized to benzoic-2-*d* acid without loss of the deuterium label by alkaline permanganate.



The deuterium was determined by combustion and estimation of the deuterium content of the water by infrared analysis. Acetophenone was prepared from benzoyl-2-*d* chloride and dimethyl cadmium as described by Cason (26).

For the synthesis of acetophenone-2,6-*d*<sub>2</sub> 4-nitrotoluene was found to be a satisfactory starting material.



With 95% deuterium sulphate at 95° C, 4-nitrotoluene underwent exchange in the 2- and 6-positions without much sulphonation. After two exchanges the compound gave no signal in the N.M.R. corresponding to the 2,6-hydrogen atoms. The signal for the 3,5-hydrogen atoms occurs at lower field. The deuterionitrotoluene was reduced with tin and hydrochloric acid; deamination and oxidation took place with complete retention of the deuterium label. The other steps were the same as for the monodeutero compound. It is noteworthy that exchange occurs at the positions predicted by the orienting effects of the methyl and nitro substituents. It is also striking that exchange proceeds so smoothly when it is considered that toluene and nitrobenzene cannot be exchanged without considerable loss due to sulphonation. It has been found that 2- and 3-nitrotoluenes exchange readily with 95% D<sub>2</sub>SO<sub>4</sub> to give 2-nitrotoluene-*d*<sub>4</sub> and 3-nitrotoluene-*d*<sub>4</sub>. In these cases no selective deuteration occurs; all positions are affected by the substituents.

The bromotoluenes were next investigated. 4-Bromotoluene exchanged its ring protons readily in 95% D<sub>2</sub>SO<sub>4</sub> at 80° C after 3 hours. Under these conditions 2-bromotoluene was sulphonated even at room temperature. However, 90% D<sub>2</sub>SO<sub>4</sub> at room temperature brought about considerable exchange and little sulphonation in 24 hours. After three equilibrations with this acid the ring proton signals in the N.M.R. spectrum were no longer visible. 3-Bromotoluene sulphonated readily in 95% D<sub>2</sub>SO<sub>4</sub> at room temperature. Exchanges with 80, 85, and 90% D<sub>2</sub>SO<sub>4</sub> at room temperature were carried out without achieving any exchange. No change was apparent in the N.M.R. spectrum of the products.

In connection with a joint project with Lecomte (27) the synthesis of several polychlorodeuterobenzenes by exchange was investigated. 1,4-Dichlorobenzene was readily exchanged in 88 mole % D<sub>2</sub>SO<sub>4</sub> as had been reported earlier by Best and Wilson (12) for the dibromo derivative. The more highly chlorinated benzenes such as the 1,3,5-trichloro, the 1,2,4,5-tetrachloro, and the pentachloro were expected to exchange under more drastic conditions due to the deactivating influence of the chlorine atoms. 1,3,5-Trichlorobenzene underwent exchange at 100° C but a temperature of 150° C was required to bring about exchange in the tetra- and penta-chlorobenzenes. Loss due to simultaneous sulphonation was, however, appreciable.

It appears that deuteration of ring protons follows the course to be expected from a consideration of the orienting effects of the substituents. The feasibility of exchange in any given case depends, however, upon the relative rates of sulphonation and exchange.

#### EXPERIMENTAL

##### *Deamination of p-Nitrobenzenediazonium Fluoborate in Isopropyl Alcohol*

*p*-Nitrobenzenediazonium fluoborate (4.0 g) prepared from *p*-nitroaniline as described by Starkey (28) was added to a suspension of 4.0 g of powdered anhydrous sodium acetate

in 10 ml of isopropyl alcohol. Rapid evolution of nitrogen took place and the reaction mixture turned very dark. After the mixture had been standing for an hour the alcohol was removed under vacuum and the residue was taken up in pentane. The pentane solution was then washed with water and dried over a pellet of alkali. The residue which remained after the pentane was distilled off was transferred to a Späth bulb and distilled. Yield of nitrobenzene, 0.5 g (35%).

*Deamination of 2-Bromoaniline in Hypophosphorous Acid*

2-Bromoaniline (6.88 g, 0.04 mole) was treated, while being stirred, in a 100-ml three-necked round-bottomed flask with 25 ml of 50% hypophosphorous acid. The solution was heated to boiling and then cooled to  $-5^{\circ}\text{C}$ . Sodium nitrite (3.0 g) was added in portions to the cold solution. Nitrogen was evolved after each addition of nitrite. The reaction mixture was stirred at  $0^{\circ}\text{C}$  for 3 hours and then poured on ice in a flask equipped for steam distillation. The distillate was taken up in ether, and the solution was dried over a pellet of alkali and then freed of solvent. The residue was purified by distillation on the vacuum line. Yield, 4.8 g (78%);  $n_D^{24.5}$ , 1.5521.

*2-Amino-3-nitrotoluene*

This compound was prepared as described in reference 19 in 53% yield.

*2-Bromo-3-nitrotoluene*

2-Amino-3-nitrotoluene (50 g, 0.3 mole) was dissolved in 160–175 ml of 48% hydrobromic acid heated on a hot plate. The solution was cooled to room temperature while 300 ml of water was slowly added. The solution was diazotized at  $-12^{\circ}\text{C}$  with 30 g of sodium nitrite dissolved in 40 ml of water and filtered. The filtrate was added in portions to a solution of cuprous bromide prepared from 60 g of copper sulphate, 24 g of copper turnings, 400 ml of water, and a solution of 60 g of potassium bromide in 270 ml of 48% hydrobromic acid. The mixture was heated for  $\frac{1}{2}$  hour on the steam bath and then distilled in steam. Yield, 57 g (81%).

*2-Bromo-3-aminotoluene*

Activated iron was prepared by mixing 240 g of iron powder and 82 ml of 48% hydrobromic acid as described in reference 20. The mixture was evaporated nearly to dryness in a vacuum evaporator at  $60^{\circ}\text{C}$ . At this stage the mass of activated iron had broken up into small balls which were removed and pulverized in a mortar. Residual moisture was removed on the vacuum line but without further shaking on a water bath at  $100^{\circ}\text{C}$ .

The reduction was carried out using 20 g of 2-bromo-3-aminotoluene as described in the reference cited above except that dioxane was used instead of benzene. The reaction mixture from the reduction was steam-distilled to remove all the dioxane after addition of 80 ml of hydrobromic acid to convert the amine to the hydrobromide. The residue was basified with 35 g of sodium hydroxide in 70 ml of water and steam distillation continued to obtain the amine. The bromotoluidine was taken up in ether in the usual way. The yield of amine recovered from a distillation in a Späth bulb at  $60^{\circ}\text{C}$  under vacuum was 65–70%;  $n_D^{23}$ , 1.6034;  $n_D^{20}$ , 1.6050.

*2-Bromo-3-amino- $d_2$ -toluene*

The amine (20.5 g, 0.11 mole) was stirred vigorously at  $80^{\circ}\text{C}$  for 8 hours with 25 ml of deuterium oxide containing one pellet of alkali. The exchanged amine was separated from the water in a separatory funnel and returned to the original flask for a second exchange. Two more exchanges were considered sufficient to replace all the amino hydrogen by deuterium. There was practically no loss during these operations.

*Deuteriohypophosphorous Acid*

Hypophosphorous acid was exchanged 10 times with deuterium oxide as described in reference 22 until the deuterium content as judged from the deuterium content of a sample of benzene-*d*, prepared by deamination of aniline-ND<sub>2</sub>, was 95.91%.

*2-Bromotoluene-3-d*

To 20 g of 2-bromo-3-amino-*d*<sub>2</sub>-toluene in a 250-ml round-bottomed flask with a side arm for a separatory funnel was added, while being cooled in ice water, 58 ml of 50% deuteriohypophosphorous acid - deuterium oxide and finally 30 ml of additional deuterium oxide. To the mixture was added, very slowly, a solution of 8.0 g of sodium nitrite in 8 ml of deuterium oxide; during the addition, the temperature was still kept around 0° C, the mixture was stirred, and the rate of nitrogen evolution was observed. The reaction mixture was protected from moisture and kept in the refrigerator overnight. In the morning all the volatile material was distilled on the vacuum line into a Stock trap. The distillate was extracted with ether and the bromotoluene recovered in the vacuum line by distillation. Yield, 10 g (55%). Mass analysis: 93.9% C<sub>7</sub>H<sub>6</sub>DBr.

In a second run from 17.6 g of amine-*d*<sub>2</sub> there was obtained 9.4 g of 2-bromotoluene-3-*d*<sub>1</sub>, *n*<sub>D</sub><sup>23</sup> 1.5539. The boiling point was 181° C. Yield, 59%. 2-Bromotoluene has *n*<sub>D</sub><sup>23</sup> 1.5540, b.p. 181° C. Mass analysis: 95.98% C<sub>7</sub>H<sub>6</sub>DBr, 4.0% C<sub>7</sub>H<sub>7</sub>Br.

*Toluene-2,3-d<sub>2</sub>*

Magnesium (0.9 g) was placed in a 100-ml two-necked round-bottomed flask equipped with a separatory funnel and a reflux condenser. The apparatus was connected to a vacuum line flamed and pumped for 1 hour to remove traces of moisture. Dry air (freed of CO<sub>2</sub> by Ascarite) was introduced at the end. A few milliliters of ether dried over sodium wire was added to the magnesium followed by 5.7 g of 2-bromotoluene-3-*d* dissolved in 20 ml of anhydrous ether. Reaction started almost at once. After the solution was stirred for about 3 hours the ether was removed under reduced pressure. The residue was cooled in a bath of ice water and deuterium oxide (7.0 ml) was added dropwise. The toluene that was formed and ether were distilled into a Stock trap. The toluene was taken up in more ether, water was separated, and the ether solution was dried. The ether was removed on the vacuum line keeping the solution at -26° C. It was condensed in a trap cooled in dry ice and acetone at -78° C. During this operation the stopcocks are set so that a little ether distills slowly but continuously from the solution. When the pressure in the system has fallen to 1 mm the residue is virtually free of ether. Yield, 2.3 g (74%). Mass analysis:

	I	II
C <sub>7</sub> H <sub>6</sub> D <sub>2</sub>	82.7%	80.1%
C <sub>7</sub> H <sub>7</sub> D	16.5%	17.8%
C <sub>7</sub> H <sub>8</sub>	0.6%	1.2%

*Benzoic-2,3-d<sub>2</sub> Acid*

Toluene-2,3-*d*<sub>2</sub> (4.5 g, 0.05 mole) and 400 ml of water were heated to boiling under a reflux condenser. Potassium permanganate (15.6 g, 0.1 mole) was added in portions over a period of 4 hours. After being heated under reflux for a further period of 4 hours the reaction mixture was filtered. The filtrate and washings were concentrated under reduced pressure to a volume of 50 ml. The solution was then acidified with concentrated hydrochloric acid (3.2 ml) and the white precipitate of benzoic-2,3-*d*<sub>2</sub> acid was filtered off and washed once with a little cold water. Yield, 4.3 g (73%); m.p. 123.4° C.

The use of a copper flask as described by Bigelow (29) did not lead to higher yields in test experiments.

#### *Benzoyl-2,3- $d_2$ Chloride*

Benzoic-2,3- $d_2$  acid (3.8 g, 0.03 mole) was heated under reflux with 4.6 g freshly distilled thionyl chloride for 2 hours. Hydrogen chloride and excess thionyl chloride were pumped off on the vacuum line and the residue was distilled into a Stock trap. Yield, 4.0 g (92%).

#### *Benzamide-2,3- $d_2$*

Benzoyl-2,3- $d_2$  chloride (4.0 g) was added slowly to 17.0 ml of concentrated ammonium hydroxide while the mixture was being stirred, and cooled in an ice bath. The solid was filtered and washed with cold water. Recrystallization from 17 ml of hot water gave 2.8 g of benzamide-2,3- $d_2$  (81%), m.p. 127–129° C.

#### *Aniline-2,3- $d_2$*

A solution of 4.2 g of potassium hydroxide in 50 ml of water in a 400-ml beaker was cooled to 0° C in an ice bath. Bromine (4.5 g) was added in one portion and the mixture was stirred until all the bromine had dissolved. Another solution of 6.0 g of potassium hydroxide in 10 ml of water was prepared. Finely powdered benzamide-2,3- $d_2$  (2.8 g, 0.02 mole) was added all at once to the potassium hypobromite, with vigorous stirring; at the same time there was added the concentrated solution of alkali prepared above. After 5 minutes all the solid had dissolved. The reaction mixture was transferred to a flask set for steam distillation and heated on the steam bath for 2 minutes. The oil which collected on the top was distilled over in a current of steam. The aniline-2,3- $d_2$  was taken up in ether, dried over alkali, filtered, and freed of solvent. The residue was distilled slowly into a trap in the vacuum line. Yield, 1.8 g (83%);  $n_D^{20}$ , 1.5844.

The deuterium content of the aniline was determined by deaminating it to benzene-1,2- $d_2$ . The mass analysis of the latter was 82.1%  $C_6H_4D_2$ , 17.1%  $C_6H_5D$ , and 0.8%  $C_6H_6$ .

#### *Deuterium Sulphate*

Deuterium sulphate for exchange reactions was prepared by the modification described below of the procedure of Best and Wilson (12).

To a condenser with ground-glass joints set for downward distillation were connected a 1-liter Claisen flask and a receiver with a side arm to which was attached a drying tube filled with glass wool and phosphorus pentoxide. The other end of the drying tube was connected by means of rubber tubing to a filter flask with a controllable leak. No lubricant was used on any of the joints but they were covered with paraffin wax on the outside.

Stabilized sulphur trioxide (300 ml) purchased from Allied Chemical of Canada, Montreal, Quebec, under the name of "Sulfan B" was poured into the distilling flask and 100 g of 99.7% deuterium oxide was weighed into the tared receiver cooled in crushed ice. When the distilling flask was gently heated and slight suction from a glass aspirator pump was applied, sulphur trioxide distilled slowly into the water.

At the end of the distillation an aliquot of deuterium sulphate was removed and analyzed by titration against *N*/10 alkali. The concentration of deuterium sulphate was then adjusted as required by addition of the appropriate amount of deuterium oxide.

#### *4-Nitrotoluene-2,6- $d_2$*

A solution of 7.0 g (0.06 mole) of 4-nitrotoluene in 25 g of 94.81% deuterium sulphate was heated at 90° C for 24 hours. The reaction mixture was cooled, and poured onto

cracked ice. The oil was extracted with ether. The ether solution was washed with water, dried over calcium chloride, and freed of solvent. The exchanged 4-nitrotoluene (5.6 g) was equilibrated twice more with fresh quantities of deuterium sulphate.

The course of the exchange was followed by examining the N.M.R. spectrum of the compound. The normal compound shows two doublets spaced 25 c.p.s. apart and 200 c.p.s. lower than the methyl signal. In the exchanged compound the doublet at higher field and therefore corresponding to the 2,6-hydrogen atoms disappeared. The spectrum was essentially unchanged after the third exchange.

#### *4-Nitrobenzoic-2,6-d<sub>2</sub> Acid*

4-Nitrotoluene-2,6-d<sub>2</sub> (19.0 g, 0.015 mole) was oxidized with potassium permanganate as described by Bigelow (29) in a Pyrex rather than a copper flask. The yield of 4-nitrobenzoic-2,6-d<sub>2</sub> acid was 17.2 g (78%).

#### *4-Aminobenzoic-2,6-d<sub>2</sub> Acid*

The 4-nitro acid was reduced with tin and hydrochloric acid as described by Vogel (30). The yield was 71% of product, m.p. 186–186.5° C.

#### *Benzoic-2,6-d<sub>2</sub> Acid*

The amino acid was diazotized and deaminated as described by Kornblum (16). The yield from 10 g of amino acid was 4.9 g (55%), m.p. 121.5–122.0° C. Analysis by combustion gave a deuterium content of 1.96 atoms. All the reactions were therefore carried out without any appreciable loss of deuterium.

#### *Benzoyl-2,6-d<sub>2</sub> Chloride*

The chloride was prepared from thionyl chloride as described above for benzoic-2,3-d<sub>2</sub> acid.

#### *Acetophenone-2,6-d<sub>2</sub>*

The acid chloride was converted into acetophenone exactly as described by Cason (26). The yield was 78% of product,  $n_D^{25}$  1.5296, m.p. 17.5° C. For normal acetophenone,  $n_D^{25}$  is 1.5307.

#### *3-Nitrotoluene-d<sub>4</sub>*

3-Nitrotoluene (6.0 g) was heated with 25 g of 97.3% deuterium sulphate for 24 hours at 75–80° C. The product was worked up as already described for the 4-nitro isomer. Recovery was 91%. Loss due to simultaneous sulphonation is therefore slight. After three exchanges there was no signal observed in the N.M.R. spectrum where the ring hydrogens occur in the light compound.

#### *2-Nitrotoluene-d<sub>4</sub>*

Nuclear proton exchange was carried out under the same conditions as for the other two isomers. The N.M.R. spectrum indicated that exchange occurred in all positions as expected though more slowly than in the other isomers.

#### *4-Bromotoluene-d<sub>4</sub>*

A mixture of 7.0 g of 4-bromotoluene (.04 mole) and 25 ml of 95.7% deuterium sulphate was stirred for 24 hours at room temperature. The exchanged 4-bromotoluene was isolated from the reaction mixture as described above. After two more exchanges the ring proton signals in the N.M.R. spectrum had disappeared while the signals due to the protons in the methyl group had their original intensity. All ring protons therefore exchange under these conditions. At 80° C the 4-bromotoluene was almost completely sulphonated after only 3 hours.



*Non-exchange of 3-Bromotoluene*

In 95.5% deuterium sulphate 3-bromotoluene is almost completely sulphonated after 3 hours at room temperature. Deuterium sulphate diluted with deuterium oxide to 80% acid did not sulphonate 3-bromotoluene at room temperature after 60 hours stirring but there was no change in the N.M.R. spectrum. Evidently no exchange had occurred. At room temperature 85% deuterium sulphate gave about 20% sulphonated product but again there was no evidence of exchange in the recovered 3-bromotoluene. In 90% deuterium sulphate at room temperature the amount of sulphonated product increased but there was still no evidence of exchange as judged from the N.M.R. spectrum. Apparently the rate of sulphonation in 3-bromotoluene is much more rapid than that of exchange.

*2-Bromotoluene- $d_4$* 

The optimum condition for exchange was to stir 2-bromotoluene at room temperature with 90% deuterium sulphate for 24 hours. More concentrated acid or higher temperature both led to extensive sulphonation. After three exchanges the signal for the ring protons had completely disappeared from the N.M.R. spectrum while the methyl proton signal retained its original intensity.

*Non-exchange in 1,2-Dimethyl-4-nitrobenzene*

In 97% deuterium sulphate the compound gave only tar. In a second attempt to bring about proton exchange the compound was stirred at room temperature in 85% deuterium sulphate. At this concentration of acid there was 40% loss due to sulphonation but no change in the N.M.R. spectrum of the recovered nitro compound.

*2-Chloronitrobenzene-3,5- $d_2$* 

2-Chloronitrobenzene (5.5 g) was heated at 70° C in 30 g of 95% deuterium sulphate for 30 hours. The product was isolated in the usual manner. There was hardly any loss due to sulphonation. After a second exchange the N.M.R. spectrum of the compound was measured. Some of the signals for the ring protons were considerably reduced. From a consideration of the orienting effects of the chlorine and nitro groups it would appear that deuteration occurred in the 3- and 5-positions.

*p-Dichlorobenzene- $d_4$* 

p-Dichlorobenzene (5.0 g) was heated with 45 g of 95% deuterium sulphate at 105° C with stirring for 6 hours. The cold reaction mixture was poured onto cracked ice and the 1,4-dichlorobenzene was filtered off and washed with water. The product obtained after two more exchanges was recrystallized from ethyl alcohol. Yield, 2.5 g (50%); m.p. 54.5° C. The N.M.R. spectrum measured in cyclohexane gave no signal for benzene ring protons.

*1,3,5-Trichlorobenzene- $d_3$* 

The conditions were essentially those employed to exchange the dichlorobenzene. Two exchanges were sufficient to cause the disappearance of the ring proton signal in the N.M.R. spectrum. The loss due to simultaneous sulphonation was again 50%.

*1,2,4,5-Tetrachlorobenzene- $d_2$* 

1,2,4,5-Tetrachlorobenzene (5.0 g) and 45 g of 97% deuterium sulphate were heated for 12 hours in a sealed tube at 150° C. The exchanged product was isolated as described for 1,4-dichlorobenzene- $d_4$  above. After three exchanges 3.2 g of the tetrachloro compound were recovered. It was recrystallized from benzene, m.p. 141.5–142° C. The signal due to the ring protons in the N.M.R. spectrum had completely disappeared.



*Pentachlorobenzene*

Pentachloronitrobenzene was reduced to pentachloroaniline in dioxane solution with activated iron and water as described above. An excellent yield of pentachloroaniline, m.p. 243–244° C, was obtained.

Pentachloroaniline was deaminated in 50% hypophosphorous acid in the presence of dioxane using isoamyl nitrite as the source of nitrous acid. One gram of the amine was dissolved in 15 ml of dioxane and 15 ml of 50% hypophosphorous acid. The stirred suspension was treated with 2 ml of isoamyl nitrite at room temperature. Nitrogen was slowly evolved for about 2 hours. The reaction mixture was poured into water and the solid filtered off. Recrystallization from ethyl alcohol gave 0.3 g of pentachlorobenzene, m.p. 84° C. The product was also purified by sublimation *in vacuo* from a bath at 70° C.

*Pentachlorobenzene-d*

The exchange was carried out with 97% deuterium sulphate as described for tetrachlorobenzene. Evidence of exchange having taken place was obtained from both N.M.R. and infrared spectra. The treatment with acid seemed to remove a small amount of impurity as the melting point of the exchanged product was raised to 86.5° C.

The compound was also prepared by deamination of pentachloroaniline in 50% deuteriohypophosphorous acid but the pentachlorobenzene-*d* contained some of the normal compound (which probably arose from H in the amino group) and had to be enriched in deuterium by exchange with deuterium sulphate just the same.

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# THE DONOR CHARACTERISTICS OF THE CARBONYL GROUP

## II. THE EFFECT OF ANGULAR VARIATIONS AT THE CARBONYL GROUP<sup>1</sup>

DENYS COOK

### ABSTRACT

The effect of variations in the angle  $X-C-X'$  (in a typical carbonyl compound  $XX'C=O$ ) on the carbonyl stretching frequency ( $\nu_{C=O}$ ) is examined in the light of recently published empirical relations between  $\nu_{C=O}$  and the ionization potential.

### INTRODUCTION

In a recent paper dealing with the donor characteristics of the carbonyl group (1) empirical relationships were demonstrated between the carbonyl stretching frequency ( $\nu_{C=O}$ ) and the ionization potential (IP). Two classes of compounds were noted: those having no group conjugated with the carbonyl group (A), and those with a group capable of such conjugation (B). The parameters of those molecules were expressed, respectively, by the equations

$$[1a] \quad \nu_{C=O} = 49.35 \text{ IP} + 1249,$$

$$[1b] \quad \nu_{C=O} = 29.20 \text{ IP} + 1409.$$

The variation of these parameters within each class was interpreted in terms of inductive and resonance effects due to the different groups attached to the carbonyl group.

The variation of IP with the carbonyl force constant  $k_{C=O}$  was considered many years ago by Walsh (2). He pointed out the relationship between IP,  $k_{C=O}$ , and  $C=O$  bond length and a parameter defining the percentage of polarity of the  $C=O$  bond. Since that time many more IP's have been accurately measured though the number of determinations of force constants of  $C=O$  bonds is still relatively small.

Previously (1) no allowance was made for the effect of variations in angle  $XCX'$  ( $\alpha$ )

(in the compound  $\begin{array}{c} X' \\ \diagdown \\ C=O \\ \diagup \\ X \end{array}$ ) on  $\nu_{C=O}$ . This will now be considered.

### VARIATION OF $\nu_{C=O}$ WITH $\alpha$

The fact that  $\nu_{C=O}$  increases on decreasing the size of a cycloalkanone ring has been known for some time (3). The phenomenon is not restricted to simple cyclic ketones, for similar compounds with heteroatoms in the ring show the same effect.

Figure 1 shows a graph of  $\nu_{C=O}$  and  $\alpha$  for a wide variety of cyclic carbonyl compounds, the data and source being listed in Table I. Points lying on the same curve in Fig. 1 are for compounds containing the same functional group, with different ring sizes depending on the number of  $-CH_2-$  groups contained therein. These lines do not have quite the same slope but get steeper from the bottom line to the top in a fairly smooth manner.

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TABLE I

Compound	$\alpha$ (degrees) <sup>a</sup>	$\nu_{C=O}$ (cm <sup>-1</sup> )	Solvent
1. $\delta$ -Valerolactone	120	1748 <sup>d</sup>	CCl <sub>4</sub>
2. $\gamma$ -Butyrolactone	108	1783 <sup>d</sup>	CCl <sub>4</sub>
3. $\beta$ -Propiolactone	94 <sup>b</sup>	1841 <sup>d</sup>	CCl <sub>4</sub>
4. 5,6-Dihydro- $\alpha$ -pyrone	120	1743 <sup>e</sup>	CCl <sub>4</sub>
5. $\Delta^{\alpha\beta}$ Butenolide	108	1785 <sup>e</sup>	CCl <sub>4</sub>
6. 2-Tetralone	120	1717 <sup>f</sup>	(Raman)
7. 2-Indanone	108	1751 <sup>f</sup>	(Raman)
8. Cyclohexanone	117 <sup>g</sup>	1716 <sup>g</sup>	CCl <sub>4</sub>
9. Cyclopentanone	108	1751 <sup>h</sup>	CCl <sub>4</sub>
10. Cyclobutanone	94	1784 <sup>i</sup>	?
11. 1-Tetralone	120	1695 <sup>h</sup>	CCl <sub>4</sub>
12. 1-Indanone	108	1723 <sup>j</sup>	CCl <sub>4</sub>
13. Cyclohexenone	120	1686 <sup>k</sup>	CCl <sub>4</sub>
14. Cyclopentenone	108	1716 <sup>l</sup>	?
15. 2-Piperidone	120	1671 <sup>h</sup>	CCl <sub>4</sub>
16. 2-Pyrrolidone	108	1700 <sup>h</sup>	CCl <sub>4</sub>

<sup>a</sup>Structural investigations have been made on only a few of the compounds in this table. For those without reference, reasonable estimates of  $\alpha$  have been made depending on the size of the ring, and on the known structure of similar compounds. This results in 120° for six-membered rings, 108° for five-membered rings, and 94° for four-membered rings. Minor discrepancies in these angles will slightly affect the slope of the lines in Fig. 1, but will not alter the conclusions.

<sup>b</sup>J. Bregman and S. H. Bauer. *J. Am. Chem. Soc.* **77**, 1955 (1955).

<sup>c</sup>C. Romers. *Rec. trav. chim.* **75**, 956 (1956).

<sup>d</sup>S. Searles, M. Tamres, and G. M. Barrow. *J. Am. Chem. Soc.* **75**, 71 (1953).

<sup>e</sup>R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith. *Can. J. Chem.* **37**, 2007 (1959).

<sup>f</sup>D. Biquard. *Bull. soc. chim. France*, **8**, 55 (1941).

<sup>g</sup>See reference 1.

<sup>h</sup>Measured in this laboratory.

<sup>i</sup>See reference 3. It is assumed that this band is for the pure liquid as these authors do not mention any solvent.

<sup>j</sup>W. M. Schubert and W. A. Sweeney. *J. Am. Chem. Soc.* **77**, 4172 (1955).

<sup>k</sup>From the files of the Spectroscopy Laboratory, Dow Chemical Company, Midland, Michigan, U.S.A.

<sup>l</sup>R. N. Jones and C. Sandorfy. *Chemical applications of spectroscopy. In Techniques of organic chemistry*, Vol. IX. Interscience Publishers, Inc., New York, 1956. p. 484.

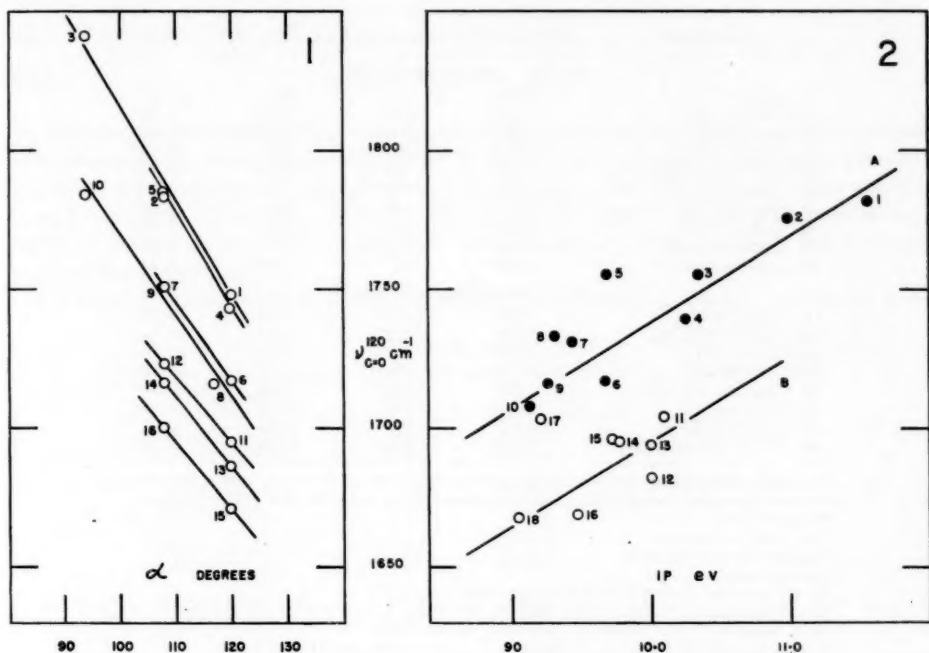
They all intersect fairly closely at one point, and a general equation has been developed which fits these lines quite closely. It has the form

$$[2] \quad \nu_{C=O}^{120} = \frac{96(\nu_{C=O} - 1439)}{(216 - \alpha)} + 1439$$

where  $\alpha$  is in degrees and  $\nu$  is in reciprocal centimeters. This equation then represents the variation of  $\nu_{C=O}$  with  $\alpha$  and should be valid whatever the nature of the group attached to the carbonyl group, for example  $-\text{CH}_2-$ ,  $-\text{O}-$ ,  $-\text{N}-$ ,  $-\text{CH}=\text{CH}-$ , etc. These groups, because of differences in inductive capacity, or ability to conjugate with the carbonyl group alter the vertical displacement in Fig. 1.

An equation similar to [2] was recently derived by Halford (4), who showed how the secular determinant could be solved to define the dependence of  $\nu_{C=O}$  on  $\alpha$ . Over the range  $\alpha = 80^\circ$  to  $\alpha = 130^\circ$  the relation was virtually linear and was described by the equation

$$[3] \quad \nu_{C=O} = 1278 + 68k_{C=O} - 2.2\alpha$$

FIG. 1. Variation of  $\nu_{C=O}^{120}$  with  $\alpha$  for compounds listed in Table I.FIG. 2. Variation of  $\nu_{C=O}^{120}$  with IP for compounds listed in Table II.

where  $k_{C=O}$  is the force constant of the carbonyl group in practical units. This equation rests on the assumptions that the masses X and X' and the force constants of the C—X' bonds are fixed.

The effect of altering  $\alpha$  then seems to have a large effect on the value of  $\nu_{C=O}$ , but as Halford's results also show, little effect on  $k_{C=O}$ . What is applicable to ring compounds as just described should apply with no loss of validity to non-cyclic carbonyl compounds. In such compounds where  $\alpha \neq 120^\circ$  because of the dependence of  $\nu_{C=O}$  on  $\alpha$ ,  $\nu_{C=O}$  may be altered even though  $k_{C=O}$  and therefore the IP and the carbon-oxygen bond distance do not alter greatly. Such alteration in  $\nu_{C=O}$  would obscure the relationship between  $\nu_{C=O}$  and IP as shown in reference 1. It is interesting therefore to adjust, by means of equation [2] the value of  $\nu_{C=O}$  to what it would be if  $\alpha$  were  $120^\circ$ . Such adjusted values are listed under the heading  $\nu_{C=O}^{120}$  in Table II for many compounds where  $\alpha$  is accurately known. The adjusted values are shown plotted against IP in Fig. 2.\*

\* Aldehydes have been excluded from this correlation. When the mass of a group attached to the carbonyl group is less than about 15 Halford (4) has shown that  $\nu_{C=O}$  then becomes mass dependent and the phase relationships of vibrations of the carbonyl group may be altered. Aldehydes, therefore, represent an extreme case, where atypical carbonyl values may be expected. For the same reason formamides and formates have been excluded. The well-known anomaly of formates having lower frequencies than acetates, when the reverse would be expected, exemplifies this point.

TABLE II

Compound	$\nu_{C=O}(cm^{-1})$	$\alpha(degrees)^a$	$\nu_{C=O}^{120}(eq. 2)$	IP(ev)
(A) Unconjugated molecules				
1. $COCl_2$	1813 <sup>b</sup>	111 <sup>f</sup>	1781	11.57 <sup>g</sup>
2. $CHCl_2COCl$	1810 <sup>b</sup>	110 <sup>g</sup>	1775	11.00 <sup>g</sup>
3. $CH_3COOH$	1768 <sup>b</sup>	116 <sup>h</sup>	1755	10.35 <sup>i</sup>
4. $CH_3COOCH_3$	1751 <sup>b</sup>	116 <sup>i</sup>	1739	10.26 <sup>j</sup>
5. $\beta$ -Propiolactone	1841 <sup>c</sup>	94 <sup>j</sup>	1755	9.70 <sup>k</sup>
6. $CH_3COCH_3$	1717 <sup>b</sup>	120 <sup>k</sup>	1717	9.69 <sup>l</sup>
7. $CH_3COC_2H_5$	1722 <sup>b</sup>	123 <sup>l</sup>	1731	9.54 <sup>m</sup>
8. $C_2H_5COC_2H_5$	1724 <sup>d</sup>	123 <sup>l</sup>	1733	9.32 <sup>n</sup>
9. Cyclopentanone	1751 <sup>d</sup>	(108) <sup>o</sup>	1716	9.27 <sup>n</sup>
10. Cyclohexanone	1716 <sup>b</sup>	117 <sup>n</sup>	1708	9.14 <sup>n</sup>
(B) Conjugated molecules				
11. $CH_2CHCHO$	1704 <sup>b</sup>	(120) <sup>o</sup>	1704	10.10 <sup>l</sup>
12. $CH_3CONHCH_3$	1700 <sup>b</sup>	113 <sup>p</sup>	1682	10.01 <sup>q</sup>
13. $CH_3COSH$	1721 <sup>d</sup>	110 <sup>g</sup>	1694	10.01 <sup>i</sup>
14. $CH_3CONH_2$	1714 <sup>b</sup>	113 <sup>p</sup>	1695	9.78 <sup>q</sup>
15. $CH_3CHCHCHO$	1696 <sup>b</sup>	(120) <sup>o</sup>	1696	9.73 <sup>r</sup>
16. Tropone	1647 <sup>e</sup>	129 <sup>r</sup>	1669	9.48 <sup>q</sup>
17. $CH_3COCOCH_3$	1717 <sup>b</sup>	115 <sup>s</sup>	1703	9.21 <sup>t</sup>
18. $(CH_3)_2CCHCOCH_3$	1697 <sup>b</sup>	(108) <sup>o</sup>	1668	9.05 <sup>t</sup>

<sup>a</sup>It is preferable to use values of  $\alpha$  from structural studies in the gas phase, i.e. electron diffraction or microwave techniques. The angles in crystals may conceivably be constrained due to lattice forces.

<sup>b</sup>See reference 1.

<sup>c</sup>See Table I, reference d.

<sup>d</sup>Measured in this laboratory.

<sup>e</sup>See reference 10.

<sup>f</sup>G. W. Robinson. J. Chem. Phys. **21**, 1741 (1953).

<sup>g</sup>See S. Mizushima *et al.* Spectrochim. Acta, **13**, 161 (1958).

<sup>h</sup>R. E. Jones and D. H. Templeton. Acta Cryst. **11**, 484 (1958).

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<sup>j</sup>See Table I, reference b.

<sup>k</sup>P. W. Allen, H. J. M. Bowen, L. E. Sutton, and O. Bastiansen. Trans. Faraday Soc. **48**, 951 (1952).

<sup>l</sup>C. Romers and J. E. G. Creutzberg. Rec. trav. chim. **75**, 331 (1956).

<sup>m</sup>Assumed, see text.

<sup>n</sup>See Table I, reference c.

<sup>o</sup>H. Mackle and L. E. Sutton. Trans. Faraday Soc. **47**, 691 (1951).

<sup>p</sup>M. Kimura and M. Aoki. Bull. Chem. Soc. Japan, **26**, 429 (1952).

<sup>q</sup>W. Gordy. J. Chem. Phys. **14**, 560 (1946).

<sup>r</sup>K. Kimura. Bull. Chem. Soc. Japan, **31**, 1051 (1958).

<sup>s</sup>J. E. LuValle and V. Schomaker. J. Am. Chem. Soc. **61**, 3520 (1939).

<sup>t</sup>K. Watanabe. J. Chem. Phys. **26**, 542 (1957), and private communication. IP under this reference are photo-ionization data. All others are electron impact data, and have been arbitrarily reduced by 0.2 ev.

<sup>u</sup>J. D. Morrison and A. J. C. Nicholson. J. Chem. Phys. **20**, 1021 (1952).

<sup>v</sup>W. C. Steele. Private communication.

<sup>w</sup>K. Higasi, I. Omura, and H. Baba. Nature, **178**, 652 (1956).

## DISCUSSION

With a few exceptions the points in Fig. 2 define two straight lines separated by more than the experimental error. The upper line, curve A, is for non-conjugated compounds, the lower, curve B, for compounds with a conjugated carbonyl group. This behavior was noted in reference 1 but by taking into account angular variations the significant difference emerges that the lines in Fig. 2 are nearly parallel, being defined by the equations (derived by the method of least squares):

$$\nu_{C=O}^{120} = 30.57 \text{ IP} + 1432,$$

$$\nu_{C=O}^{120} = 30.07 \text{ IP} + 1394.$$

Adjusting these equations so that they have the same slope leads to

$$[4a] \quad \nu_{C=O}^{120} = 30.50 \text{ IP} + 1433,$$

$$[4b] \quad \nu_{C=O}^{120} = 30.50 \text{ IP} + 1390.$$

In the previous treatment (1) curves A and B converged at low  $\nu_{C=O}$  values. The present case seems to be more satisfactory since it means that conjugation has approximately the same effect on the carbonyl frequency in all cases. The difference between the two lines at constant IP is about  $43 \text{ cm}^{-1}$ . This is a little larger than the difference in  $\nu_{C=O}$  between non-conjugated and conjugated compounds, i.e.  $\sim 35 \text{ cm}^{-1}$  (5), but a simple explanation is possible.

Consider the compounds in Table III, differing only in having a single or a double bond

TABLE III<sup>a</sup>

Compound	$\nu_{C=O}$	IP	$\Delta\nu_{C=O}$	$\Delta\text{IP}$
$\text{CH}_3\text{COCH}_2\text{CH}_3$	1722	9.54	33	-0.17
$\text{CH}_3\text{COCHCH}_3$	1689	9.71		
$\text{HCOCH}_2\text{CH}_3$	1738	9.86	34	-0.24
$\text{HCOCHCH}_3$	1704	10.10		
$\text{HOOCCH}_2\text{CH}_3$	1758	10.27	37	-0.43
$\text{HOOCCHCH}_3$	1721	10.70		
$\text{HCOCH}_2\text{CH}_2\text{CH}_3$	1729	9.81	33	+0.08
$\text{HCOCHCHCH}_3$	1696	9.73		
Average			34	-0.19

<sup>a</sup>Data from reference 1.

in the  $\alpha$  position to the carbonyl group. The change from non-conjugated to conjugated compound decreases  $\nu_{C=O}$  by  $34 \text{ cm}^{-1}$  but the IP increases by 0.19 ev. From equation [4] 0.19 ev corresponds to  $6 \text{ cm}^{-1}$ . The  $35 \text{ cm}^{-1}$  difference is therefore made up of two quantities of opposite sign, of approximate magnitudes  $43 \text{ cm}^{-1}$  and  $6 \text{ cm}^{-1}$ .

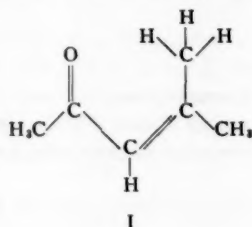
The conjugated molecules that have been considered here all have atomic skeletons that are planar so that there is no steric resistance to conjugation which would obscure the relation between IP and  $\nu_{C=O}$ . One compound which illustrates this point is benzophenone. By analogy with the known structure of substituted benzophenones, for example, 4,4'-dichlorobenzophenone (6) and 4,4'-dimethoxybenzophenone (7), in which the phenyl rings are about  $38^\circ$  out of the  $\text{C}=\text{O}$  plane, there will be inhibited conjugation

between the  $\text{C}=\text{O}$  group and the ring. For benzophenone  $\nu_{C=O} = 1668 \text{ cm}^{-1}$ . Assuming  $\alpha = 125^\circ$ , then  $\nu_{C=O}^{120} = 1681 \text{ cm}^{-1}$ . The IP is 9.00 ev and according to the equations [4a] and [4b] would require  $\nu_{C=O}^{120}$  to be 1665 and  $1708 \text{ cm}^{-1}$  respectively. The actual value of  $\nu_{C=O}^{120}$  lies in between these two values but nearer the conjugated value (curve B).

Two further molecules can be considered in detail, since they exemplify the arguments put forward here. The first is mesityl oxide, which when previously considered (1) did not lie on the appropriate curve B for a conjugated ketone, but was very close to curve A for non-conjugated compounds. Steric strain due to bulky methyl groups was invoked to account for the non-coplanarity of the double bonds and the consequent belief that

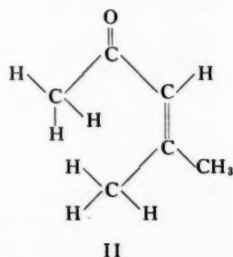


the compound was properly placed on curve A. A more plausible explanation is now possible. The suggested model is planar and in the *cis* configuration I. This is in keeping with enhanced intensity of the C=C vibration at  $1624\text{ cm}^{-1}$  (8) and dipole moment studies (9). The interference between the methyl group and the carbonyl oxygen is relieved



by decreasing ( $\alpha$ ) thus bending the carbonyl oxygen away from the methyl group. From a study of molecular models (Stuart-Briegleb) a decrease in  $\alpha$  of about  $12^\circ$  would give ample clearance. Applying equation [2] again,  $\Delta\nu$  would be  $31\text{ cm}^{-1}$ . The effect of the change in angle then is to increase  $\nu_{\text{C=O}}$  by  $31\text{ cm}^{-1}$ .  $\nu_{\text{C=O}}^{120}$  is therefore  $1668\text{ cm}^{-1}$  and taking  $\text{IP} = 9.05\text{ eV}$  Fig. 2 shows that the point lies very close to curve B for conjugated molecules.

It is interesting to apply similar reasoning to the *trans* structure II. In this case the



interference is between the methyl groups. To relieve this situation  $\alpha$  would have to increase and the value of  $\nu_{\text{C=O}}$  would be lower than that corresponding to  $\alpha = 120^\circ$ . In applying the correction therefore  $\nu_{\text{C=O}}^{120}$  would be greater than  $1697\text{ cm}^{-1}$ , and the point for mesityl oxide would be further from the curve than before.

The second molecule is tropone. Its carbonyl frequency is  $1642\text{ cm}^{-1}$  (10). This value must be adjusted since it is for the pure liquid, which is well known to be invariably lower than that for a dilute solution in an inert solvent like  $\text{CCl}_4$ . The gas phase value is  $1652\text{ cm}^{-1}$  (11). If a value of  $\nu_{\text{C=O}} = 1647\text{ cm}^{-1}$  is assumed then  $\nu_{\text{C=O}}^{120}$  now comes to  $1669\text{ cm}^{-1}$ . Figure 2 shows how much more closely tropone approaches curve B than the unadjusted value.

The origin of the angle-dependent frequency shift has been made clear in some recent work by Overend and Scherer (12). After calculating the force constants of C=O bonds in carbonyl halides the surprising result was established that  $k_{\text{C=O}}$  for  $\text{COF}_2$  was little different from that of  $\text{COCl}_2$ , 12.85 and  $12.61\text{ md/\AA}$  respectively, while there was a difference of  $101\text{ cm}^{-1}$  in  $\nu_{\text{C=O}}$ . On calculation of the relative displacement of the atoms in the normal vibrations of the carbonyl halides these authors found that as the C=O

bond stretched the carbon atom moved back into the two fluorine atoms. The C—F bonds were therefore compressed and the FCF angle increased. For  $\text{COF}_2$  where  $k_{\text{C-F}} = 4.5 \text{ md/\AA}$  the resistance to these motions results in the greater frequency for  $\text{COF}_2$  compared with  $\text{COCl}_2$ , where  $k_{\text{C-Cl}} = 2.0 \text{ md/\AA}$ .

Carbon-carbon single bonds have force constants of the order of  $4 \text{ md/\AA}$ , quite comparable to the C—F bond. The C—O force constant is of similar magnitude. Consequently in the compounds discussed in this paper there will be an appreciable effect similar to that in the carbonyl halides. Moreover, it will be obvious that as the angle  $\text{XCX}'$  decreases this effect will get larger since the movement of the C atom during a carbonyl stretching vibration will be more nearly along the line of the C—X atom.

A similar conclusion was reached by Bratöz and Besainou (13). These authors started with a frequency value for an isolated carbonyl group then added increments depending on the type of group attached to the C=O group. The largest contributions arose from mechanical interaction between the carbon or oxygen atom next to the carbonyl group. This was shown to get larger as  $\alpha$  became smaller, as has been shown above too.

No three-membered cyclic saturated ketone is known, unfortunately, so that it has not been possible to see, whether there is any point at which equation [2] breaks down. It has been shown that for propiolactone, the smallest ring compound for which both the IP and  $\nu_{\text{C=O}}$  are known, a great improvement is achieved by use of equation [2] but that it is far from being a good correlation.\* While no direct test of a three-membered cyclic ketone is possible due to lack of data, some approximations can be calculated for a substituted cyclopropanone recently synthesized. This is 2,3-diphenylcyclopropanone whose carbonyl frequency is  $1852 \text{ cm}^{-1}$  (14). Allowing about  $40 \text{ cm}^{-1}$  for the effect of conjugation and unsaturation the hypothetical cyclopropanone might have a frequency of  $1892 \text{ cm}^{-1}$ . Assuming  $\alpha = 60^\circ$ ,  $\nu_{\text{C=O}}^{120}$  is  $1718 \text{ cm}^{-1}$  in quite good agreement with saturated aliphatic ketones.

#### CONCLUSIONS

The present work goes some way toward an understanding of the large variations in carbonyl frequencies. From the results presented, however, it is apparent that there remain some unsatisfactory anomalies. Until, however, accurate force constants for a large number of molecules have been worked out, involving prodigious labor, methods such as the present one offer some hope of reducing the problem.

#### ACKNOWLEDGMENTS

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# A PROTON MAGNETIC RESONANCE INVESTIGATION OF ROTATIONAL ISOMERISM IN 1,1,2,2-TETRACHLORO-1-FLUOROETHANE<sup>1</sup>

R. J. ABRAHAM<sup>2</sup> AND H. J. BERNSTEIN

## ABSTRACT

The doublet separation in the proton resonance spectrum of the liquid was measured from -53 to 100° C. From the variation of the separation with temperature approximate values of the trans and gauche HF coupling constants were obtained. The values of  $\Delta H = 400$  cal/mole and  $\Delta S = 0$  are also consistent with the data.

Nuclear magnetic resonance has been used with some success in the investigation of problems concerned with rotation about single bonds (1, 2, 3). Data from other techniques, such as vibrational spectroscopic, for information regarding  $\Delta H$ , the enthalpy difference of the rotamers, and the assumption that the entropy difference is negligible, has usually gone into the derivation of the coupling constants.

The purpose of this work was to investigate the simplest possible proton magnetic resonance spectrum, the spacing of which depends on the relative concentrations of the rotational isomers.  $\text{CFCl}_2\cdot\text{CHCl}_2^*$  is admirably suited for this since the proton magnetic resonance is a simple doublet. The doublet separation was measured with a Varian spectrometer at a radio frequency of 40 Mc/s as accurately as possible (to  $\pm 0.02$  cycle/second) by the wiggle beat (4) method in a temperature-controlled ( $\pm 1^\circ$ ) cell which has been previously described (5). The results are shown in Fig. 1 and Table I.

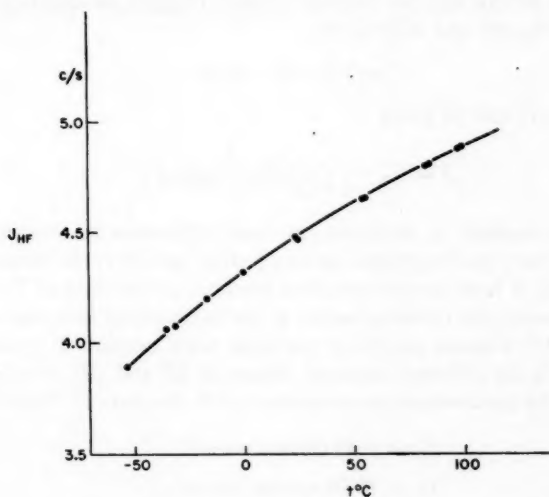


FIG. 1.

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\*We are indebted to R. Kagarise for supplying this compound.

TABLE I

$t, ^\circ\text{C}$	$J_{\text{obs}}$	$J_{\text{calc}}$	Obs. - calc.
-53	3.89	3.88	0.01
-35	4.06	4.05	0.01
-31	4.07 <sub>a</sub>	4.08	-0.005
-16.5	4.20	4.20	0.00
0	4.32	4.30	0.02
24	4.48	4.48	0.00
25	4.47	4.49	-0.02
54.4	4.65	4.66	-0.01
55.2	4.65 <sub>a</sub>	4.66	-0.005
83.2	4.80	4.80	0.00
85.0	4.81	4.82	-0.01
98	4.89	4.89	-0.01
99.7	4.89	4.89	0.00

The molecule  $\text{CFCl}_2 \cdot \text{CHCl}_2$  exists in three conformations, one in which H and F are trans oriented and a pair of mirror image gauche forms. If we denote the fraction of the trans form as  $p$ , that of each gauche form is  $(1-p)/2$ , and the total fraction of molecules in the gauche form is  $1-p$ , at any temperature

$$[1] \quad \frac{p}{1-p} = \frac{1}{2}e^{-\Delta F/RT} = \frac{1}{2}e^{\Delta S/R} \cdot e^{-\Delta H/RT}$$

where the factor  $\frac{1}{2}$  takes into account the two mirror image magnetically equivalent gauche forms. The observed spacing (i.e. coupling constant  $J$  in cycles/second) for this compound depends on the number average of the coupling constants in the trans ( $J_T$ ) and gauche ( $J_G$ ) forms (6) and is given by

$$[2] \quad J = pJ_T + (1-p)J_G.$$

Eliminating  $p$  from [1] and [2] gives

$$J = J_T - \frac{J_T - J_G}{1 + \frac{1}{2}e^{\Delta S/R} \cdot e^{-\Delta H/RT}}.$$

In principle it is possible to evaluate the four unknowns in this equation ( $J_T$ ,  $J_G$ ,  $\Delta S$ ,  $\Delta H$ ). However, very much greater accuracy than  $\pm 0.02$  cycle/second in a measurement of  $J$  is required. A least squares solution attempt on the data of Table I turned out to be rather complicated due to the presence of the exponential function and did not give an acceptable result.\* Various graphical methods were employed consisting chiefly of solving for  $J_T$  and  $J_G$  for different assumed values of  $\Delta S$  and  $\Delta H$ . It turns out that the following values of the parameters are consistent with the data of Table I:

$$\begin{aligned} J_G &= 1.03 \text{ cycles/second,} \\ J_T &= 18.08 \text{ cycles/second,} \\ \Delta S &= 0, \\ \Delta H &= 400 \text{ cal/mole.} \end{aligned}$$

The values of  $J$ , calculated with the above, give the column of calculated  $J$  values in

\*Because of the small available experimental range, the curve in Fig. 1 can be described within the experimental error by a three-parameter function. For this reason the least squares solution to determine all four parameters is not significant and when carried out leads to physically unacceptable results.

Table I. The value of  $\Delta S = 0$  is not inconsistent with the very small entropy difference in the gas phase (7) for the rotamers of 1,2-dichloroethane. The fact that  $\Delta H$  is positive shows that the gauche isomer is more stable than the trans isomer. This information and the value of  $\Delta H = 400$  cal/mole are in agreement with the infrared studies on this molecule (8).

The values found for the coupling constants, entropy difference, and enthalpy difference are considered reliable to about 10%. Very much higher accuracy in the measurement of  $J$ , or a very much extended temperature range, would be required to improve on these numbers. There is no doubt, however, that  $J_T$  is considerably larger than  $J_G$ . This is analogous to the situation in substituted ethylenes (9) where the trans HF coupling constant is larger than the cis. Also, it is interesting to note that for the HH coupling constants in substituted ethanes (3),  $J_T \gg J_G$ . Presumably the same reasons (10) are valid for HF coupling constants that are invoked to explain the higher trans HH coupling constant.

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## AN INFRARED STUDY OF THE ADSORPTION OF BUTENES ON SURFACES OF POROUS VYCOR GLASS<sup>1</sup>

L. H. LITTLE,<sup>2</sup> H. E. KLAUSER,<sup>3</sup> AND C. H. AMBERG

### ABSTRACT

The adsorption and reactions of the four butenes on porous Vycor glass at room temperature have been studied by infrared spectroscopy. Initial adsorption was rapid and was found to perturb the surface hydroxyl groups of the glass. In the case of the *n*-butenes rapid isomerization took place at room temperature. In addition to this the adsorbate spectra showed the occurrence of a slower reaction which led to an increase in saturated C—H groupings. C<sub>4</sub> and higher compounds were shown to have formed; on outgassing at room temperature small amounts of cracking products were collected. The polymerization of isobutene was particularly rapid. Experiments at low coverage ( $\theta \sim 0.001$ – $0.002$ ) gave identical initial spectra for the *n*-butenes. These were discussed in terms of possible models for butene adsorption. A reduction in the alumina and zirconia content of the glass by acid leaching resulted in decreased rates of isomerization and polymerization, suggesting that one or both of these oxides are at least partially responsible for the activity of the glass. A pure silica aerogel was almost completely inactive. Quantitative measurements of the spectra of several monoolefins in solution were made for comparison with the surface species, in particular with respect to their molar intensities of absorption.

### INTRODUCTION

The adsorption of olefins on catalytically active surfaces is a prerequisite to subsequent isomerization, polymerization, and cracking reactions (1). For instance, in a recent publication MacIver, Zabor, and Emmett (2) discussed the chemisorption, followed by cracking and polymerization, of 1-butene and 1-octene on silica-alumina cracking catalysts; their data were consistent with the formation of carbonium ion intermediates. Few other studies of the adsorption of butenes or higher olefins on similar surfaces have appeared in the literature, probably because of the complexity of the resulting systems.

It was the object of the present investigation to study the adsorption of butenes on porous Vycor glass by infrared spectroscopy. The adsorbent was suitable owing to its high transmission in the region of  $3.4 \mu$ , where the bands due to C—H stretching modes in hydrocarbons occur. Moreover, it had a high surface area, so that even at low fractional coverages, sufficiently large quantities of adsorbed material remained in the sample to ensure good infrared sensitivity. An extensive review of infrared spectra of adsorbed molecules was given by Eischens and Pliskin (3).

### EXPERIMENTAL

The samples of porous Vycor glass (Corning Glass, No. 7930) were generally in the form of plates 1 mm thick, 2 cm wide, and 5 cm long; 2-mm and 0.1-mm plates were used in some instances. They were cleaned by heating to 400° C in oxygen, cooled, weighed, and then transferred to the combined infrared and adsorption cell.

One of these cells consisted of a silica test tube of 1.5 mm wall thickness, 15 cm length, and 2.4 cm diameter. It was mounted in a vertical position with the infrared light beam passing through its walls. An infrared gas cell of 10-cm path length and fitted with sodium chloride windows was attached at the upper end of the silica tube through a

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ground-glass joint. When required, this cell could be placed in the light beam. The whole assembly could be connected to a vacuum and gas-handling system. Another type of cell of 10-cm path length and 4 cm in diameter was wound with a heater along about 5 cm of its central section. Sodium chloride windows were attached at the ends by means of silicone resin (Dow Corning, No. 996); temperatures of at least 150° C could thus be tolerated at the windows. A flattened glass tube with just enough clearance for 2-mm Vycor plates was mounted to the cell in a vertical position. At its upper end there was provided a short piece of glass rod led horizontally into the cell through a ground-glass joint. Sample plates were suspended from it on a spun-glass thread; by rotating the rod they could be wound up and out of the infrared beam for the determination of vapor-phase spectra. A sketch of this cell is shown in Fig. 1.

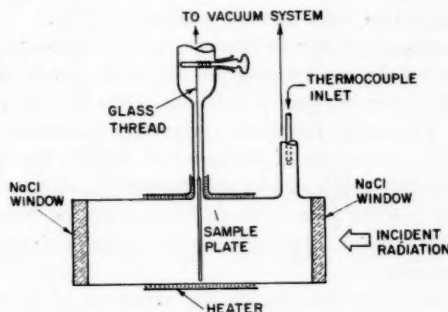


FIG. 1. Sketch of cell showing windlass arrangement for sample plate.

Samples were outgassed at 300° and cooled to room temperature, after which the background spectrum was recorded. The silica test tube transmitted in the same spectral region as the Vycor plates and thus did not interfere. After admission of gas to the sample the spectrum composed of background, adsorbate, and gas phase was recorded, as well as that of the gas phase alone. The latter was necessary to correct the adsorbate spectrum, where indicated, and was also useful for purposes of identifying reaction products. With the silica cell, corrections were usually not more than 10% of the absorption of the surface species; at low coverage they were completely negligible. All experiments were performed at room temperature.

The spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer fitted with either a sodium chloride or a calcium fluoride prism, or alternately on a Beckman IR4 spectrophotometer with a lithium fluoride prism. All spectra reproduced in the diagrams are tracings from experimental records, while all data in the tables under the heading "Adsorbate" refer to the surface phase only. The time shown for each spectrum refers to time after gas admission.

The following spectral parameters were measured or computed for absorption bands of surface species: frequency  $\nu$  cm<sup>-1</sup>; optical density  $D = \log_{10} J_0/J$ , where  $J_0/J$  is the ratio of incident to transmitted radiant energy at a given frequency; extinction coefficient  $\epsilon = D/cl$  mole<sup>-1</sup> liter cm<sup>-1</sup>, where  $c$  is the concentration of adsorbate in terms of moles of butene per liter of sample (external dimensions) and  $l$  is the total path length through the sample in centimeters; integral band intensity  $I = \int D d\nu$  cm<sup>-1</sup> and molar intensity  $\bar{I} = I/cl$  mole<sup>-1</sup> liter cm<sup>-2</sup>. As long as  $c$  refers to actual butenes adsorbed on the glass

surface,  $\bar{I}$  represents the true value for butenes and is, within the experimental limits, an absolute intensity. However, when part or all of the butenes have polymerized, then  $\bar{I}$  is a composite of all species present, expressed in molar concentrations of  $C_4$ . We have used these values for comparisons with pure butenes, or higher monoolefins similarly expressed in terms of  $C_4$  concentrations (see Appendix).

Errors in the determination of  $\bar{I}$  were  $\pm 15\%$  at the worst, but usually somewhat better. Apart from errors inherent in the integrating procedure (Simpson's rule), the chief contributing factor was the uncertainty involved in constructing the background spectrum. This spectrum was subject to small changes from that originally measured on the pure adsorbent; these were due to (a) perturbation of the adsorbent by the adsorbate and (b) the occasional removal of the cell from the spectrometer and subsequent repositioning. Consistency between the three different prisms was about  $\pm 5\%$ . Errors in the volume adsorbed were usually less than  $\pm 2\%$ .

Neither extinction coefficients nor intensities were corrected for finite spectrometer resolving power, because of the overlapping nature of the bands. Bands above  $3000\text{ cm}^{-1}$  were resolved graphically from the group of bands below for the purpose of determining their relative intensity. The errors involved, depending somewhat on the separation and intensities of the bands, were usually of the order of  $\pm 10\%$ , but in some cases higher.

The frequencies, indicated vertically in the figures, have uncertainties of  $\pm 10\text{ cm}^{-1}$  for sodium chloride and  $\pm 3\text{ cm}^{-1}$  for lithium fluoride optics. Spectral slit widths were, respectively,  $18\text{ cm}^{-1}$  and  $6\text{ cm}^{-1}$ . For some bands extinction coefficients were added in parentheses in the diagrams.

Supplementary analyses were undertaken by means of mass spectrometry and gas-liquid chromatography. Vapor-phase and weakly sorbed materials were collected by condensation into a liquid nitrogen trap. More severe stages of outgassing involved the additional use of a vacuum pump for periods of up to 20 hours and finally the application of heat to the sample.

A modified Vycor adsorbent was prepared by leaching the glass for 6 hours in boiling concentrated nitric acid and by carefully washing it. Spectrographic analyses showed that, of the chief constituents other than silica, boron had remained unchanged, while aluminum and zirconium, both present in approximately equal amounts, had decreased to about one-half their former value. Subsequent quantitative analysis showed  $B_2O_3$  to have remained constant at  $2.1\%$  while  $R_2O_3$  had decreased from  $0.89\%$  to  $0.36\%$ . The B.E.T. surface areas, determined with nitrogen at  $-195^\circ\text{C}$ , had changed from  $165\text{ m}^2/\text{g}$  to  $148\text{ m}^2/\text{g}$ .

The silica aerogel (Cab-O-Sil, Godfrey L. Cabot, Inc.) used had a surface area of  $166\text{ m}^2/\text{g}$ . An infrared transparent plate was prepared from it by pressing at  $40\text{ tons/in}^2$ .

The preparation of a sample of Vycor glass with black nickel oxide dispersed in its pores has been previously described (4).

## RESULTS AND DISCUSSION

### (i) Adsorption of *n*-Butenes on Porous Vycor Glass at $\theta \sim 0.1$

Rapid adsorption of *n*-butenes at an initial pressure of about  $2\text{ cm Hg}$  occurred on a Vycor sample in the first 15- to 20-minute period; this was followed by a much slower uptake. Coverage in this series of experiments was of the order of  $0.1$  monolayer (see Section (ii)). In the early stages, adsorption of a predominant fraction of the surface molecules was of a physical nature (including interactions due to hydrogen bonding). This was inferred from the similarity between the initial spectra and the corresponding

spectra in carbon tetrachloride solution (Fig. 8). For example, the characteristic absorption bands associated with olefinic C—H stretching vibrations were clearly discernible in either case (1-butene:  $3080\text{ cm}^{-1}$ , Fig. 2(a); 2-butenes:  $3020\text{ cm}^{-1}$ , Figs. 2(b) and 2(c)). Moreover, the ratios of olefinic to total C—H band intensities (Table I) were approximately the same as the corresponding ones in carbon tetrachloride solution (Table VI). In addition to this the adsorbed molecules perturbed the surface hydroxyl groups of the glass with the result that the  $\nu_{\text{OH}}$  band was broadened and displaced to lower frequencies; these changes are generally caused by hydrogen bonding (5) and may be attributable to the formation of such bonds involving surface hydroxyls and the

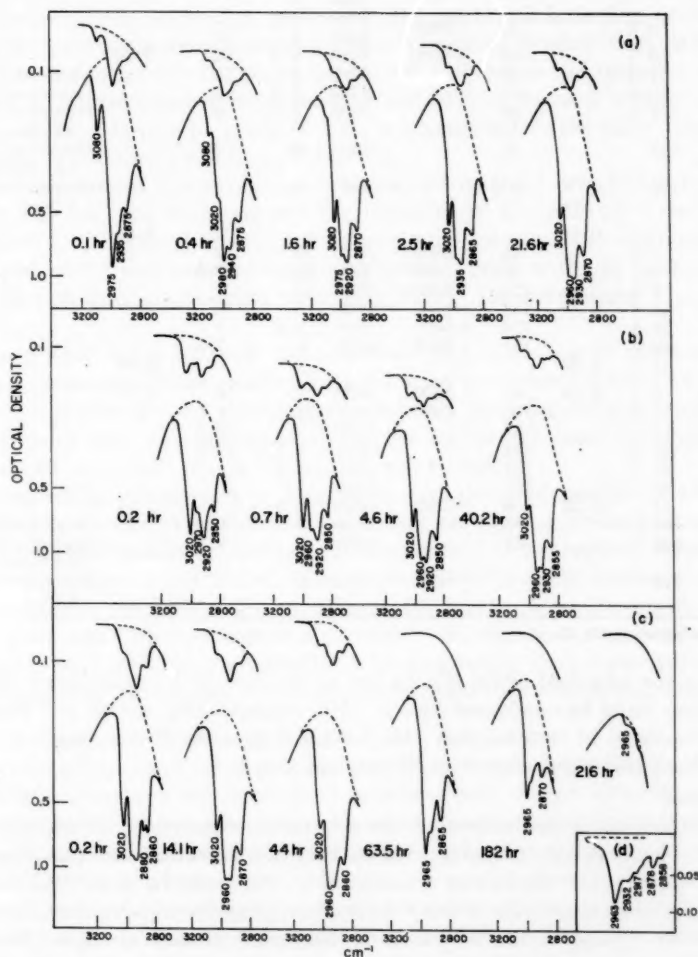


FIG. 2. Adsorption of *n*-butenes on porous Vycor glass at  $\theta \sim 0.1$ : (a) 1-butene, (b) *cis*-2-butene, (c) *trans*-2-butene; the last three spectra represent successive stages of outgassing. The upper spectrum in all cases is that of the vapor phase. (d) Polymeric residue from *trans*-2-butene at higher resolution; calculated spectrum of surface phase only. Optics: NaCl for (a), (b), and (c); LiF for (d).

TABLE I  
Adsorption of *n*-butenes on porous Vycor glass at  $\theta \sim 0.1$

Compound	Time, hours	Adsorbate					Gas		Outgassing procedure
		Total (as butenes)		Olefinic bands		Intensity % of total	Pressure, cm Hg		
		Conc., moles l. <sup>-1</sup>	$I_p$ , cm <sup>-1</sup>	$I_p$ , mole <sup>-1</sup> l. cm <sup>-2</sup>	$\nu$ ,* cm <sup>-1</sup>				
1-Butene	0.1	0.22						2.88	
	0.2		123	5400	3080	7	112		
					3020	4			
	0.6		132	~5800	3080	4.5	111		
					3020	5			
	10.3		162	~5700	3020	8.5	95	2.70	
	11.3		88		3020	5	10		Condensed 5 minutes
	13.9		52		3020	3.5	0		Condensed 2 hours
	39.5		46		3020	2.5	0		Heated to 100° for 12 minutes
	112		21		3020	0	0		Heated to 120° for 45 minutes
	128		5.5		3020	0	0		Heated to 160° for 1 hour
<i>cis</i> -2-Butene	0.1	0.18						1.50	
	0.2		94	5200	3020	29	12		
	0.7		96	5300	3020	24	10.5		
	4.6		121	~5500	3020	15	9		
	16.0		133	~6600	3020	8	8		
	16.4		123	~5600	3020	8.5	8		
	40.2		151	6900	3020	5	7.5		
	41.7	0.21						0.96	
	<i>trans</i> -2-Butene	0.2	0.19	95	5000	3020	16	16	1.72
0.8			100	5200	3020	14	16		
14.1			132		3020	7	10.5		
20.9			138		3020	8.5	12.5		
21.1			131		3020	7.5			
43			157		3020	7	10		
44		0.22	158	~7300	3020	6.5		1.14	
63.5			73		3020	2	0		Condensed 6.5 hours
182			37		3020	0	0		Heated to 100° for 3.5 hours
	216		2		3020	0	0		Heated to 155° for 6.5 hours

\*Exact frequencies given in Fig. 2.

$\pi$ -electrons of the adsorbed olefin (6). In the early stages of an experiment 70% of the adsorbed phase could be condensed into a liquid nitrogen trap within ~5 minutes; the condensate consisted of butenes only. By further outgassing it was possible to restore the surface hydroxyl band almost to its original shape.

#### Isomerization

Rapid double-bond isomerization of the *n*-butenes occurred on adsorption at room temperature. This is readily demonstrated by both the adsorbate and gas-phase spectra (Fig. 2). For instance, in the case of 1-butene (Fig. 2(a)), the band at 3080 cm<sup>-1</sup> due to the asymmetric stretching mode of the =CH<sub>2</sub> group progressively decreased in intensity, while the =CH— band of the 2-butenes at 3020 cm<sup>-1</sup> became stronger. At the same time the ratio of the olefinic to total C—H band intensity increased from the initial 8–10% of 1-butene to 14.5% (estimated from Table I and confirmed by subsequent runs), i.e. it approached the higher values of a predominantly *cis*-*trans* mixture (Table VI).

Two hours after admission of any one of the *n*-butenes the contour of the spectra of



the gas phase in contact with the surface showed these to consist largely of *trans*-2-butene by comparison with the spectra of the pure gases in Fig. 8. GLC analyses gave percentages of 3.5, 71.5, and 25.0 respectively for 1-butene, *trans*- and *cis*-2-butene both for the residual gas phase and for material removed from the sample by outgassing. The corresponding equilibrium values at 25° C calculated from the data of Rossini (7) are 2.42, 74.24, and 23.34%.

#### *Polymerization and Cracking*

After the isomerization process had reached equilibrium, the contour of the bands changed with further standing. The olefinic C—H band at 3020  $\text{cm}^{-1}$  decreased, while the band at 2965  $\text{cm}^{-1}$  due to saturated C—H groupings, increased in intensity. These results were consistent with a process of polymerization occurring on the surface, i.e. with a decrease in the number of double bonds per total number of bonds in the molecule. The process continued with standing and after 40 hours the intensity of the band at 3020  $\text{cm}^{-1}$  had decreased from between 10 and 20% of the total to only 5% (for typical results, see *cis*-2-butene in Table I). This is approximately the value found for 2-octene in carbon tetrachloride solution (Table VI).

When the system was evacuated, unsaturated material, which was found to contain largely butenes, was removed and the intensity of the 3020  $\text{cm}^{-1}$  band decreased to about 2–3% of the total intensity. This would indicate that the remaining material was composed of  $\text{C}_8$  and possibly larger molecules. Along with the butenes, monoolefins with the following composition were identified in the condensate:  $\text{C}_3$ ,  $\text{C}_5$ ,  $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_8$ , and  $\text{C}_9$ .

In a further series of tests, the adsorbate was taken up in pentane, the resulting solution concentrated and analyzed by GLC on an Apiezon column. Various available pure monoolefins showed good linear correlation on a logarithmic elution time versus boiling point plot. On this basis a complex mixture of some 12 constituents boiling between 80° and 210° ( $\text{C}_6$  to  $\text{C}_{12}$  region) was eluted.

By increasing the severity of outgassing after the condensation of what were largely butenes, the material removed from the surface contained a greater proportion of cracked and polymerized products. Intensity measurements of the residual adsorbate after outgassing for 1 hour at 50–150° C showed that 80–90% of the surface C—H groups had been removed. No bands due to unsaturated species were detectable. The bands at 2965, 2930, and 2870  $\text{cm}^{-1}$  due to saturated C—H vibrations suggested a preponderance of methyl over methylene groups, i.e. branched rather than linear polymers. The ratio of the heights of these bands did not appear to change with outgassing (see Section (vi)).

#### (ii) *Low-coverage Adsorption of n-Butenes, $\theta \sim 0.001$ – $0.002$*

In the spectra described above, the strong bands due to physically adsorbed material in the early stages of the adsorption process would almost certainly mask any bands due to a possible chemisorbed butene species and thus preclude its identification. After polymerization has set in, the intense bands of the polymeric surface species are again liable to interfere. It was thought that optimum conditions might be attained by working at low initial pressures. Small doses of butene were therefore admitted so that within 1–2 minutes the pressure had dropped to below 0.01 mm Hg. The initial measurements were made within 5–15 minutes after gas admission. Using the nitrogen area of 165  $\text{m}^2/\text{g}$  and a molecular area for butenes of 31  $\text{\AA}^2$  we estimate a coverage of 0.001–0.002 of a monolayer in these experiments (Fig. 3, Table II). Similarly, the coverage in the experiments described in the previous section was in the region of  $\theta = 0.1$ .



TABLE II  
Adsorption of butenes on porous Vycor glass at  $\theta \sim 0.001-0.002$

Compound	Time, hours	Adsorbate*				
		Total (as butenes)			Olefinic bands	
		Conc., moles l. <sup>-1</sup>	$I$ , cm <sup>-1</sup>	$I$ , mole <sup>-1</sup> l. cm <sup>-2</sup>	$\nu$ , <sup>†</sup> cm <sup>-1</sup>	Intensity % of total
1-Butene	0.3	$1.7 \times 10^{-3}$	5	4500	3020	12.5
	1.3		4.5	4200	3020	11
	23.5		5	4500	3020	10.5
	50.5		4.5	4200	3020	11.5
	143.5		5.5	4900	3020	4
<i>cis</i> -2-Butene	0.1	$2.3 \times 10^{-3}$	3.5	2500	3020	11.5
	3		4	3000	3020	14
	23.9		4	3000	3020	12
	112.8		5	3500	3020	8
	162		5.5	3800	3020	2
<i>trans</i> -2-Butene	0.2	$2.4 \times 10^{-3}$	5.5	3800	3020	12.5
	4.8		4.5	3200	3020	11
	22.2		5	3600	3020	9.5
	29.5		5.5	3800	3020	7.5
	53.8		5.5	3800	3020	5.5
Isobutene	120		6	4300	3020	1.5
	0.1	$2.8 \times 10^{-3}$	8.5	5000	—	0
	16.5		11	6400	—	0
	117		9.5	5500	—	0

\*Gas phase not observable. †Exact frequencies given in Fig. 3.

Because of the small amount of adsorbed material it was necessary to record the spectra through six plates, each 1 mm thick, in order to obtain bands of measurable intensity. The absorption and reflection from six plates of Vycor glass was itself appreciable in the spectral region being studied. Moreover, the spectrum of the samples was steeply sloping such as to make observation of weak bands superimposed upon this background very difficult. This was corrected by placing a similar but evacuated cell containing six 1-mm Vycor plates in the reference beam. Spectra were then recorded relative to this compensating cell. Figure 3(a) demonstrates the effect, and clearly emphasizes the necessity, of compensating for glass absorption in this case.

Within 5 minutes after admitting the *n*-butenes to the samples the spectra showed that the surface species were identical for the three *n*-butenes; presumably rapid isomerization had occurred on the surface. The band at 3020 cm<sup>-1</sup> characteristic of the =CH— group was found in all three cases, i.e. it had replaced the =CH<sub>2</sub> band at 3080 cm<sup>-1</sup> in the case of the 1-butene. Possible models for this surface species will be discussed below. The spectra for *cis*-2-butene are not reproduced in Fig. 3, since they differ in no way from the other two.

The molar intensities of absorption were well below the values for adsorbed butenes at the higher coverage of  $\theta \sim 0.1$ . It is interesting to note, though, that the fractional intensity of the band at 3020 cm<sup>-1</sup> had remained in the same range as that found for  $\theta \sim 0.1$  after the attainment of isomerization equilibrium.

The slow increase in total band intensity noticeable after a period of several days (Table II) was indicative of slow polymerization. The increase was particularly marked in the 2965 cm<sup>-1</sup> band; it was matched by an equally slow decrease of the 3020 cm<sup>-1</sup> band. Furthermore the contours of the final spectra closely resembled those of the polymerized species found at  $\theta \sim 0.1$  (Fig. 2).

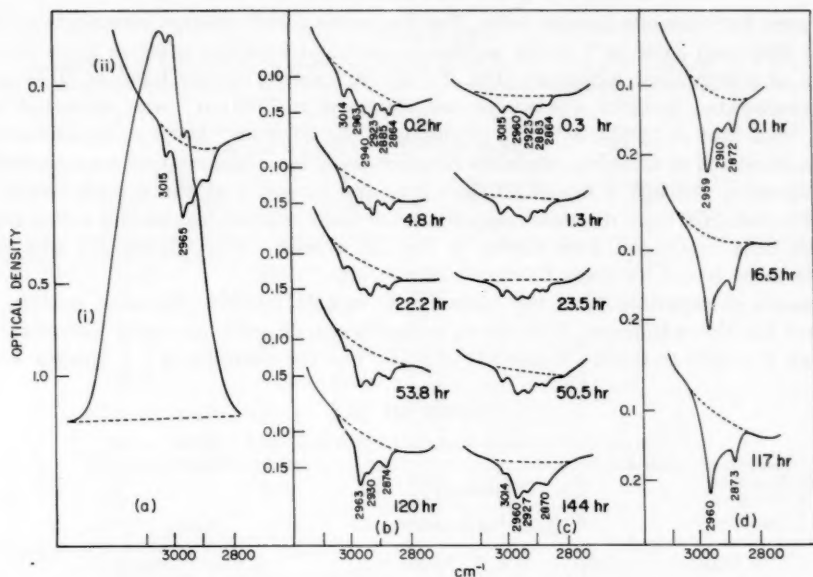


FIG. 3. Adsorption of butenes on porous Vycor glass at  $\theta \sim 0.001-0.002$ : (a) spectrum (i) before and (ii) after compensating for background absorption, (b) *trans*-2-butene, (c) 1-butene, (d) isobutene. Optics: LiF.

(iii) *Adsorption of Isobutene on Porous Vycor Glass*

When sufficient isobutene for 0.03 monolayer coverage was admitted to the Vycor sample, adsorption was very rapid. Within 5 minutes the entire dose had adsorbed and no gas spectrum was detectable. The following observations confirm the view that a very fast polymerization process had occurred.

The spectrum of the surface species (Fig. 4) showed very intense absorption bands

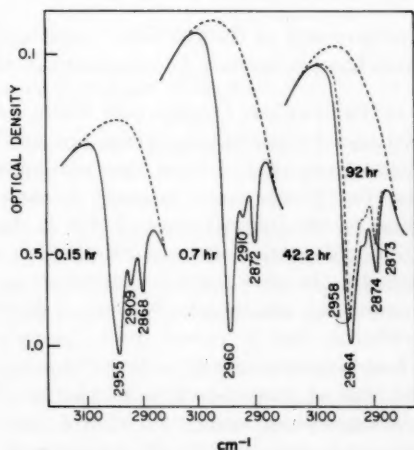


FIG. 4. Adsorption of isobutene on porous Vycor glass at  $\theta \sim 0.03$ . The broken line (92 hours) shows spectrum after outgassing. Optics: LiF.

of saturated hydrocarbon groups only. The frequencies and relative intensities of the bands at 2960 and 2870  $\text{cm}^{-1}$  in the isobutene spectrum were the same as those in the spectrum of polymerized *n*-butenes (Fig. 2); in the former case the band at 3020  $\text{cm}^{-1}$  due to unsaturated material was absent and the band at 2910  $\text{cm}^{-1}$  was somewhat less resolved from that at 2960  $\text{cm}^{-1}$ . The intensity of the 2910  $\text{cm}^{-1}$  band in the isobutene spectrum decreased on standing, while the total intensity remained relatively unchanged.

On outgassing through a liquid nitrogen trap the intensity of the surface bands at 2960, 2910, and 2870  $\text{cm}^{-1}$  decreased slightly, while their relative heights did not change. The gases thus condensed were shown to contain cracked and polymerized products similar to those found for the *n*-butenes.

The results of experiments at low coverage ( $\theta = 0.002$ ) follow the same pattern as was found for the *n*-butenes. There was a significant decrease in molar intensity in going from  $\theta = 0.03$  to 0.002 (Tables III and II), but the contours of the spectra were

TABLE III  
Adsorption of isobutene on porous Vycor glass at  $\theta \sim 0.03$

Time, hours	Adsorbate		Gas		
	Total (as butene)*				
	Conc., moles $\text{l}^{-1}$	$I$ , $\text{cm}^{-1}$	$I$ , $\text{mole}^{-1} \text{l. cm}^{-2}$	$I$ , $\text{cm}^{-1}$	Pressure, $\text{cm Hg}$
0.1	0.068				0.07
0.15		70	10000	0	0.00
0.2		65	9200	0	
0.4		54	7600	0	
0.7		54	7600	0	
1.1		62	8900	0	
42.2		70	9300	0	
42.2		67	8900	0	
43.6		75	10000	0	
43.9					
92†	0.073	52		0	

\*Olefinic bands not observable. †Sample outgassed for 30 hours.

identical (Figs. 4 and 3). The intensity of the 2910  $\text{cm}^{-1}$  band again decreased. Eischens and Pliskin have assigned this band to tertiary C—H groups in surface molecules (3).

(iv) *Adsorption of Butenes on Porous Glass Leached with Nitric Acid*

Eight minutes after admitting 1-butene to a sample of the acid-leached glass to attain a coverage of  $\theta \sim 0.1$ , the spectrum (Fig. 5) was very similar to that of 1-butene in carbon tetrachloride solution (Fig. 8); the molar intensity of the surface material (Table IV) was in the same range as on the original glass (Table I), both being considerably less than the value in solution. Adsorption was rapid during the first 20 minutes, after which it slowed down markedly. In this respect adsorption proceeded likewise in a manner similar to that on unleached specimens. In contrast to this, however, the time to reach isomerization equilibrium had increased from approximately 1 to 50 hours. Appreciable isomerization had occurred already after 6 hours, the surface spectrum having changed to resemble that of *trans*-2-butene in solution (Fig. 8). Isomerization was similarly indicated by the gas-phase spectrum. After 4 days relatively little polymerization had occurred. This can be seen in Table IV, for instance, by the high fractional intensity of the 3020  $\text{cm}^{-1}$  band. After the butenes had been removed by condensation,

TABLE IV  
Adsorption of butenes on acid-leached Vycor glass at  $\theta \sim 0.1$ ; also 1-butene at  $\theta \sim 0.01$

Adsorbate									
Compound	Time, hours	Total (as butenes)			Olefinic bands		Gas		Outgassing procedure
		Conc., moles l. <sup>-1</sup>	<i>I</i> , cm <sup>-1</sup>	<i>I</i> , mole <sup>-1</sup> l. cm <sup>-2</sup>	$\nu$ ,* cm <sup>-1</sup>	Intensity % of total	<i>I</i> , cm <sup>-1</sup>	Pressure, cm Hg	
1-Butene	0.1	0.17							2.22
	0.15		97	5500	3080	7	16.5		
	0.3		87	5000	3080	7.5	16.5		
	6.4		92	5250	3080	3	14		
					3020	13			
	16.9		81	4600	3080	0.5	16		
					3020	22			
	51.3	0.18	110	5900	3080	0.5	14		2.07
	89	0.19	113	5850	3020	14.5	13		
	91	0.19							
	93		15.5		3020	13.5	0		
	117		6		3020	5	0		
	141		4.5		3020	4.5	0		
1-Butene	0.05	0.011							0.07
	0.1		7	4900	3080	1.5	0		
	0.3		8	4800	3080	1	0		0.00
					3020	12.5			
	0.5	0.018							
	0.7		8	4200	3020	15	0		
	2.1		8.5	4500	3020	15.5	0		
	5.2		9.5	5000	3020	13	0		
	21		9.5	5000	3020	13	0		
	<i>cis</i> -2-Butene	0.3	0.20						
0.35		81		3900	3020	23.5	15		
0.9			84	4150	3020	22.5	15		
<i>trans</i> -2-Butene	0.25	0.18							2.12
	0.3		89	4700	3020	15	18.5		
	0.6		80	4300	3020	15.5	18.5		
Isobutene	0.1	0.19							1.71
	0.2		110	5650	3077	5	8		
	0.8	0.23							1.32

\*Frequencies exact for isobutene only; all others given in Figs. 5-7.

weak bands remained, the contours of which (Fig. 5) were similar to those of the polymerized material remaining on unleached samples under comparable conditions (Fig. 2). The band intensities were, however, one order of magnitude less.

In a second experiment with 1-butene the effect of reducing the coverage to  $\theta \sim 0.01$  was examined (Table IV, Fig. 6). The outstanding feature of the results was the shortening of the period within which the 3080 cm<sup>-1</sup> band was replaced by that at 3020 cm<sup>-1</sup>. While formerly the 3080 cm<sup>-1</sup> band was still recognizable after 2 days, it had now completely disappeared after 40 minutes.

The adsorption of *trans*- and *cis*-2-butene was studied at  $\theta \sim 0.1$  (Table IV); spectra (Fig. 7) were recorded at 20 and 40 minutes after gas admission, when isomerization was negligible. The molar intensities were again considerably less than the corresponding values in solution (Fig. 8). However, both ratios of olefinic to total C—H band intensities agreed remarkably well with the solution values.

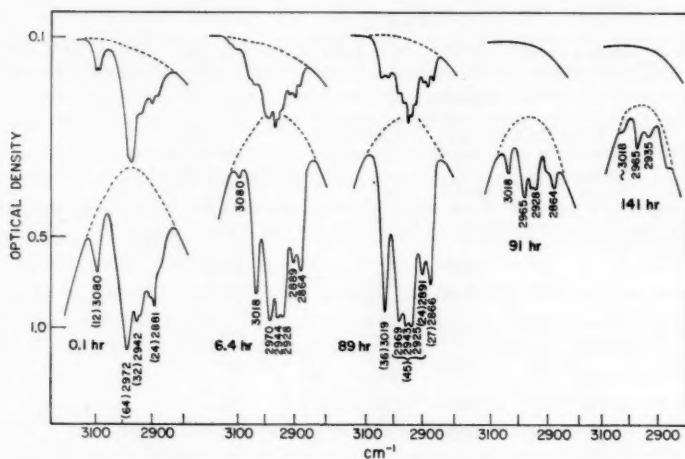


FIG. 5. Adsorption of 1-butene on acid-leached Vycor glass at  $\theta \sim 0.1$ . The upper spectra are those of the vapor phase. The last two spectra represent successive stages of outgassing. Optics: LiF.

Isobutene (Table IV) reacted far more rapidly than the *n*-butenes on the leached sample; as a result of this the gas uptake at a comparable initial pressure was greater. The fractional intensity of the  $3080\text{ cm}^{-1}$  band even at 12 minutes after gas admission was about one-half the value in carbon tetrachloride solution (Table VI). It may be presumed from this that again considerable polymerization had taken place, although the rate of disappearance of the  $3080\text{ cm}^{-1}$  band was far slower than with the unleached glass.

(v) *Adsorption Sites. Structure of Adsorbed Butenes*

The 10% decrease in surface area which occurred during leaching could not by itself

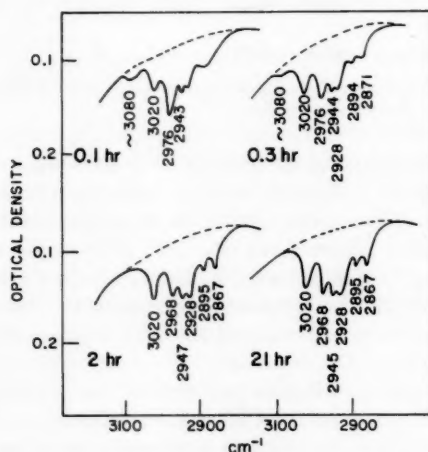


FIG. 6. Adsorption of 1-butene on acid-leached Vycor glass at  $\theta \sim 0.01$ . Optics: LiF.

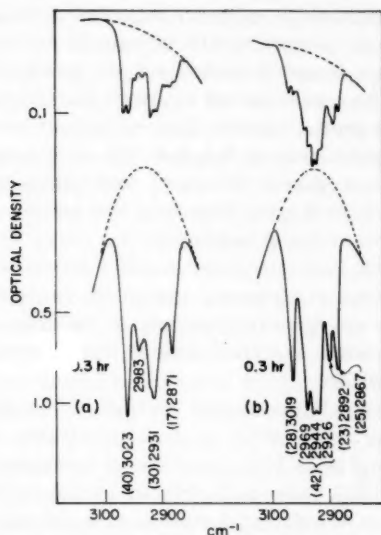


FIG. 7. Initial spectra of (a) *cis*- and (b) *trans*-2-butene on acid-leached Vycor glass at  $\theta \sim 0.1$ . The upper spectra are those of the vapor phase. Optics: LiF.

account for the marked decrease observed in the isomerization and polymerization rates.

In an effort to characterize more closely the source of these changes in activity, we attempted to observe the effect on the  $\nu_{OH}$  band of the surface hydroxyl groups by the nitric acid leaching. This was not feasible with samples 1 mm thick, because they absorb completely all radiation between  $3800\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ . However, 0.1-mm samples transmit throughout this region and permit a complete study of the  $\nu_{OH}$  band.

No significant change in the optical density and half-width of the  $\nu_{OH}$  band after acid treatment was found.

Previous workers with Vycor glass (8) and similar materials (9) have discussed a second type of surface site, apart from the silanol group. This was tentatively ascribed to the Si-O-Si grouping or, more specifically, silicon atoms in the surface.

From the evidence presented in our case it is almost certain that the alumina (and probably also the zirconia) was involved in the adsorption and reaction of the butenes. If our examination of the change in the hydroxyl structure with leaching was sufficiently sensitive, then this would exclude a predominant role being played by surface hydroxyls in the activity changes discussed in the previous section. The metal or oxide sites would themselves form the adsorption centers or, possibly, act as proton acceptors for carbonium ions formed on neighboring surface hydroxyls. Removal of the centers would then result in decreased reaction rates at a given butene coverage. An extreme sample of this would be represented by the results of some experiments which we have conducted with a pure silica aerogel (Cab-O-Sil). The surface area of the silica was comparable to that of the Vycor glass. It had no  $R_2O_3$  content, but an appreciable concentration of free surface hydroxyls. After standing in contact with butene for about 1 month, isomerization was barely perceptible; no polymeric species were detected.



On the other hand, the spectroscopic evidence regarding the  $\nu_{OH}$  band is by no means unambiguous and the following picture would be equally consistent with the changes observed after leaching. If we accept a carbonium ion mechanism to be operative in the reactions (1), then adsorption on a surface hydroxyl (Si-OH or Al-OH) is a plausible first step towards subsequent proton transfer and carbonium ion formation. Of interest in this connection are the recent data of Scholze (10), who found that the content of free hydroxyls in alkali silicate glasses increased with  $Al_2O_3$  content, although  $B_2O_3$  showed the same effect to a high degree. However, our present data do not permit us to distinguish between these various possibilities.

It is instructive to estimate the concentration of "active sites" relative to initial butene coverage in the various experiments described. Such estimates must remain approximate inasmuch as we are ignorant not only of the exact nature of the sites, but also of their energy distributions. We shall confine ourselves therefore to estimating  $R_2O_3$  concentrations in the surface.

Taking the  $R_2O_3$  content (see Experimental Section) to be equally divided between alumina and zirconia, we arrive at a total (Al + Zr) concentration of 0.18 gram-atom/liter of Vycor. The density of the glass is 1.45 g/cc.\* For a homogeneous dispersion of  $R_2O_3$  we estimate about 15% or 0.027 gram-atom/liter to reside on the surface. This is by analogy with the silica surface-to-bulk ratio arrived at under the assumption of a  $10 \text{ \AA}^2$  area for repeat units of silica in the surface. After leaching, 40% of the original  $R_2O_3$  remained in the glass, corresponding to a maximum of 0.011 gram-atom/liter in the surface, but probably very much less.

1-Butene is the most suitable of the *n*-butenes with which to follow the process of isomerization. Not only is almost all of it converted, but it is clearly recognizable down to low concentrations in butene mixtures, owing to the well-resolved band at  $3080 \text{ cm}^{-1}$ . In Table V we have grouped together data for the adsorption of 1-butene in the order

TABLE V  
Correlation of 1-butene to (Al + Zr) ratio with activity and initial molar intensity

Mole ratio, 1-butene:(Al+Zr)	Glass	$\sim \theta$	$3080 \text{ cm}^{-1}$ band disappeared at $\sim$ hours	$I_{\text{initial}}$ , $\text{mole}^{-1} \text{ l. cm}^{-2}$
15	Leached	0.1	50	5500
8	Original	0.1	1	5400
1	Leached	0.01	0.7	4900
0.06	Original	0.001	<0.1	3000-5000*

\*Estimated from the identical spectra arising from *n*-butenes at low coverage.

of decreasing ratios of initial adsorbate to "active sites". These follow the same trend as the time it takes for isomerization to come to equilibrium. This correlation supports the view that the removal of  $R_2O_3$  is the primary cause of the deactivation of the glass.

As a possible alternative to leaching out "active sites" we attempted to block them. (a) Unsupported nickel oxide is considered to be inactive as a butene isomerization catalyst below  $400^\circ$  (11). We found that when 1-butene was adsorbed on Vycor impregnated with  $\sim 2\%$  nickel oxide, neither the isomerization nor the polymerization rates were significantly affected and the system behaved in every respect like that shown in

\*Corning Glass, Specifications.

Fig. 2. Although this result is inconclusive, it throws additional light on the work of one of us (L.H.L.): Ethylene, which did not polymerize on Vycor alone, did so when nickel oxide was present, giving rise to a *trans*-2-butene spectrum (4). On continued standing, the butene polymerized further. We are now able to infer that it was the Vycor support rather than the nickel oxide which had catalyzed subsequent  $C_4$  polymerization. (b) We performed a series of experiments involving several successive cycles of adsorption and partial desorption. This was done by admitting either a fresh dose of pure butene for each cycle, or else by readmitting the previously isomerized mixture. In no case were we able to detect inhibition of isomerization or polymerization activity due to polymer build-up on the surface. Since in all experiments the initial ratio of butene:(Al + Zr) was of the order of 10, our results tend to support the mechanism which involves the enhancement of surface hydroxyls by the  $R_2O_3$  constituents. In other words the estimated ratio of 10 must be several times too small and far more extensive polymer coverage would be required for deactivation.

The last column in Table V shows the initial molar intensities for 1-butene. There is an apparent decrease with preponderance of "active sites" per mole of adsorbed butene, i.e. when the spectrum originates from an increasingly large fraction of strongly sorbed molecules in the adsorbed layer. This is in line with the lower values generally found in our case in the surface phase when compared with values in a solvent medium, but should nevertheless be regarded with caution because of the large probable error.

In this connection it is interesting to note that if the spectra in Fig. 3 ( $\theta \sim 0.001$ ) are indeed those of predominantly *trans*-2-butene as was suggested by their contours, then the fractional intensities of the  $3020\text{ cm}^{-1}$  band (Table II) are 30% lower than would be expected from the values in solution (Table VI). Barring the early onset of polymerization, which we consider unlikely, this indicates that the perturbation of the molecule by the surface was intensified about the double bond. Conversely, the agreement between the values in Table IV (leached glass,  $\theta \sim 0.1$ ) and those in Table VI could be explained by the fact that the relevant surface spectra were chiefly determined by the large proportion of weakly sorbed butenes in the surface layer.

Within our limits of accuracy, extinction coefficients experienced the same fractional decrease from solution to surface as did the molar intensities, i.e. we could not observe any significant changes in band shape (compare corresponding numbers in parentheses in Figs. 5, 7, and 8). In most cases frequencies were not significantly different within the limits of error, although for *trans*-2-butene we have observed an apparently real shift in the olefinic stretching band from  $3021\text{ cm}^{-1}$  in solution to  $3019$  and  $3015\text{ cm}^{-1}$  at high and low surface coverages respectively. Small shifts of this type are commonly encountered in condensations from gaseous to liquid-type phases, as can be seen in Fig. 8, where the decrease from gas to solution for the butenes was in the range  $7\text{--}9\text{ cm}^{-1}$ .

All the available evidence cited so far, as well as the probable short life of reaction intermediates (2), favors some type of physical adsorption to have been responsible for the observed spectra. However, we cannot entirely exclude the possibility that the spectra are those of a chemisorbed butene species, if not composites of both types. As discussed in Section (ii), the low-coverage spectra are the most suitable for examining this question. From these we may draw certain conclusions as to the possible structure of a spectrally predominant species.

(a) Since a band appeared at  $3020\text{ cm}^{-1}$ , the species must contain one or more of the

groups  $\diagup\text{C}=\text{C}\diagdown\text{H}$ ,  $\text{H}\diagdown\text{C}=\text{C}\diagup\text{H}$ , or  $\text{H}\diagup\text{C}=\text{C}\diagdown\text{H}$ . This would exclude adsorption by such mechanisms as



or



where S indicates a surface site.

(b) The 10–12% intensity ratio of the  $3020\text{ cm}^{-1}$  band would make a polymeric species unlikely (see Table VI). It would probably also exclude a structure such as



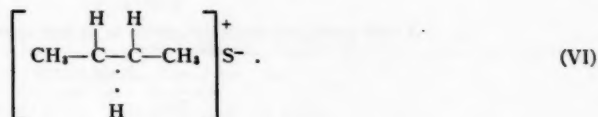
where only one H-atom is associated with the olefinic carbons (see 2-methyl-2-butene, Table VI). However, a species formed by the dissociation of hydrogen from an  $\alpha$ -methyl group would be consistent with the observed spectra



(c) The carbonium ion frequently postulated as the intermediate species in double-bond isomerization and polymerization reactions may be considered as existing in two stable forms (1). One of these is the  $\sigma$ -complex (12)



Only bands in the region of saturated C—H absorption might be expected from such a structure, i.e. it would not be consistent with the spectra in Fig. 3. However, evidence given below in connection with (VI) would suggest retention of some double-bond character in (V) as well. Exclusion of any species does not, of course, rule out participation in the processes under discussion, unobservable though it may be by spectroscopic means. The second form is the  $\pi$ -complex (12)



Recently Powell and Sheppard (13) have determined the infrared spectra of a number of platinum and palladium complexes with ethylene. In their case weak bands in the C—H stretching region and frequencies similar to those of gaseous ethylene were observed. Earlier Chatt and Duncanson (14) had found that the olefinic character in the spectra of a number of metal-olefin  $\pi$ -complexes had been essentially preserved. We quote this work to show that a relatively stable  $\pi$ -complex with the surface might still be expected to give rise to absorption above 3000  $\text{cm}^{-1}$  and would be compatible with the spectra in Fig. 3. A weaker type of interaction with surface hydroxyls, which also involves the  $\pi$ -electrons of the olefinic double bond and which can be regarded as hydrogen bonding, we have already discussed in Section (i). Presumably this latter type of bond would represent the first stage in carbonium ion formation.

(vi) *Band Assignments for Adsorbed Species*

In the past, bands at 2965  $\text{cm}^{-1}$  and 2870  $\text{cm}^{-1}$  have been assigned to vibrations of methyl groups and bands at 2930  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  to vibrations of methylene groups for spectra of adsorbed molecules (3, 4), although Eischens and Pliskin (3) have commented on the uncertainties in making such assignments. They are made by analogy with spectra of normal liquid hydrocarbons (15) and are probably correct for large adsorbed molecules. On the other hand, for such molecules as *trans*-2-butene, the occurrence of bands at 2930 and 2850  $\text{cm}^{-1}$  clearly cannot indicate the presence of methylene groups. The multiplicity of bands in the spectra of small unsaturated molecules arises *inter alia* from overtones of C—H deformation vibrations.

A further difficulty arises from the fact that large regions of the spectrum may be obscured by intense absorption bands of the adsorbent. Thus confirmation of a likely structure by observing bands in other spectral regions may not be possible, and structural conclusions have to depend on observations of a limited number of bands.

For assigning structures to adsorbed molecules we have confined ourselves to comparing the spectra with analogous ones in solution. The only exception to this has been the assignment of bands occurring at wave numbers higher than 3000  $\text{cm}^{-1}$  to unsaturated groupings. This was substantiated by quantitative intensity measurements as well as by GC and mass spectrometric analyses after desorption of the materials responsible for those bands.

#### APPENDIX

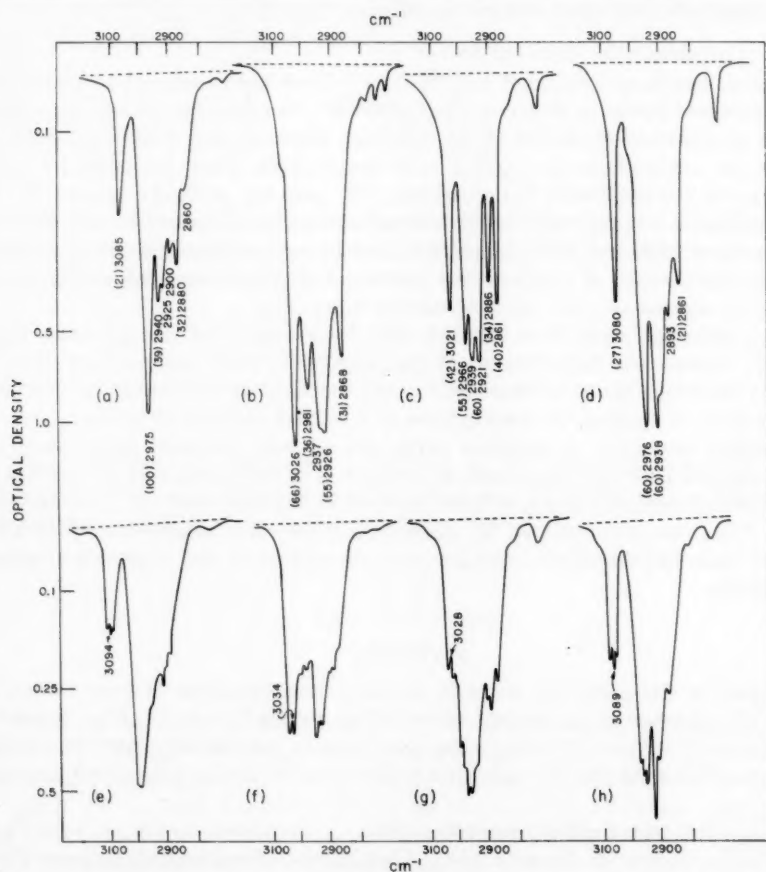
As indicated in the preceding sections, spectral determinations of pure olefins have been made for purposes of comparison with surface species (Table VI, Figs. 8 and 9).

Butene solutions were analyzed by mass spectrometry immediately after the recording of a spectrum. Following this, the spectrum was re-recorded to check for possible evaporation losses.

All butenes used were Phillips Research Grade. Of the higher olefins, all were Phillips Research Grade, except for 2-octene and 2,4,4-trimethyl-2-pentene which were Phillips

TABLE VI  
 C—H stretching modes of olefins in carbon tetrachloride solution

Compound	Conc., moles l. <sup>-1</sup>	Total bands		Olefinic bands	
		<i>I</i> (real), mole <sup>-1</sup> l. cm <sup>-2</sup>	<i>I</i> (as C <sub>4</sub> )	$\nu$ , cm <sup>-1</sup>	Intensity % of total
1-Butene	1.00	7350	7350	3085	9.5
<i>cis</i> -2-Butene	0.97	6850	6850	3026	22
<i>trans</i> -2-Butene	1.16	6750	6750	3021	16
Isobutene	1.97	6350	6350	3080	12.5
2-Methyl-1-butene	0.54	9550	7650	3069	6.5
2-Methyl-2-butene	0.69	10500	8400	3027	5.0
Cyclopentene	0.58	10500	8400	3056	9.0
1-Hexene	0.36	13700	9150	3076	4.5
				~3020	~0.5
Tetramethylethylene	0.52	14200	9500	—	0.0
1-Octene	0.66	20300	10200	3082	3.0
				~3020	~1.5
2-Octene	0.27	19600	9800	3015	4.5
2,4,4-Trimethyl-2-pentene	0.37	19000	9500	~3020	~1.5


 FIG. 8. Spectra of (a) 1-butene, (b) *cis*-2-butene, (c) *trans*-2-butene, and (d) isobutene in carbon tetrachloride solution. The corresponding vapor spectra (e)-(h) are shown in the same order; pressure, 2.1 cm Hg; path length, 5 cm. Optics: LiF.

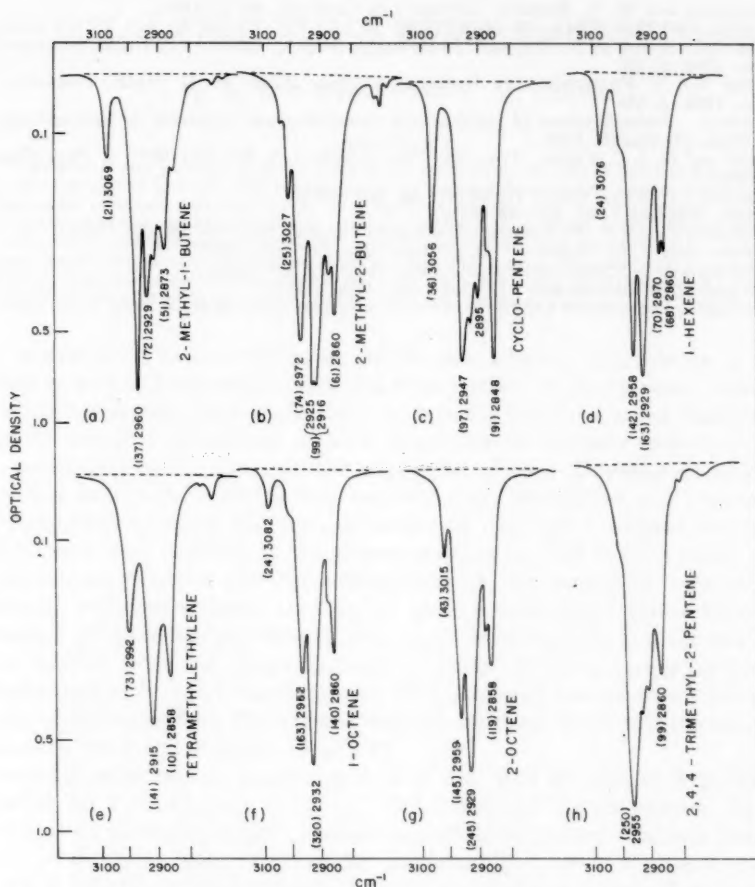


FIG. 9. Spectra of C<sub>6</sub>-C<sub>8</sub> monoolefins in carbon tetrachloride solution. Optics: LiF.

Technical grade (95 mole% minimum). Their purity was checked by mass spectra; these were in good agreement with API values. A small trace of hexene was found in the 2-methyl-1-butene. Tetramethylethylene was a NBS high-purity sample.

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# OXIDATION OF WHEAT STARCH WITH ALKALINE HYPOCHLORITE<sup>1</sup>

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## ABSTRACT

The starch was oxidized with 5.5 base molar equivalents of 0.43 *M* calcium hypochlorite kept near pH 12 and 20°. The rate of oxidation was consistent with the occurrence of two first-order reactions differing in rate by a factor of 10, the more rapid of which consumed about 4 moles of hypochlorite for each C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> unit actually oxidized. Oxalic acid (0.21 mole) and perhaps carbonic acid (>0.17 mole) were formed directly, but it was necessary to hydrolyze the product in order to liberate D-glucose (0.4 mole), glyoxylic acid (0.03 mole), D-erythronic acid (0.11 mole), mesotartaric acid (0.02 mole), D-tartaric acid (0.02 mole), L-tartaric acid (0.01 mole), D-glucuronic acid (0.004 mole), and probably tartronic acid (>0.03 mole).

The oxidation of various species of starch with alkaline hypochlorite, a process of industrial as well as academic interest, has been studied for many years. Reviews (1, 2) of the subject show that most of the early interest was attracted to the changes produced by various amounts of oxidant in such properties as viscosity and copper-reducing power, ease of retrogradation, and the adsorption of dyes. Degradation products were isolated and identified in only a very few instances. McKillican and Purves (3) more recently obtained evidence that hypochlorous acid near pH 4 oxidized wheat starch in the second and sixth positions of the glucose residues to yield in part 2-keto and uronic acid derivatives. Whistler and his collaborators (4, 5), employing corn amylose and amylopectin with hypochlorite kept at 25° and at various pH values between 3 and 13, dialyzed the products and showed that both the dialyzable and the non-dialyzable portions yielded D-glucose, glyoxylic acid, D-erythronic acid, and D-erythronolactone after hydrolysis with acid. Oxidations near pH 7 produced the maximum amount (about 0.3 mole) of glyoxylic acid. The present research provided additional information about the course of the reaction at pH 12 and 20°.

Preliminary experiments, employing 0.12 *M* and 0.06 *M* calcium hypochlorite with mole ratios per C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> unit of 1:1 or 1:0.5, confirmed the observation (5) that such oxidations were exceedingly slow. Sodium hypochlorite yielded solutions from which it was more difficult to isolate the organic products. The use of a greater excess (mole ratio, 5.5:1) of a more concentrated (0.43 *M*) hypochlorite increased the speed of the oxidation to a convenient value, and had the additional advantage that the rate constant for the disappearance of hypochlorite would tend to follow the first-order kinetic equation. A semilogarithmic plot of the data (Fig. 1, plot A) became linear after about 76 hours and could be represented by the equation  $\log 0.24/(0.24-b) = 2.2 \times 10^{-3}T$ , where *b* was the concentration of hypochlorite consumed at time *T*, the units being moles, liters, and hours. Substitution of values of *T* between zero and 76 hours then yielded values of *b* from which, by difference from the observed values, the corresponding data *b*<sub>1</sub> for the initial, fast reaction could be calculated. These data (plot B) also fitted a first-order equation,  $\log 0.19/(0.19-b_1) = 2.2 \pm 0.1 \times 10^{-2}T$ .

The above calculations suggested that the oxidation of starch with hypochlorite at pH 12 consisted of a relatively rapid reaction consuming 2.34 moles of hypochlorite

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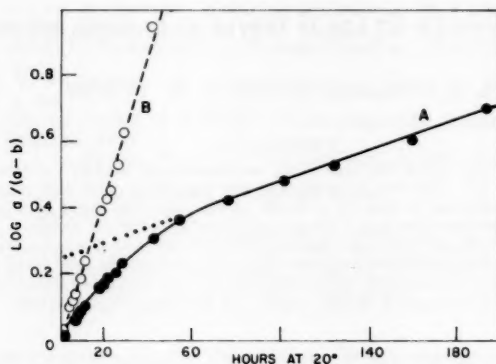


FIG. 1. Rate of oxidation of 0.183 base molar starch solution at pH 12 and 20° with 1.33 volumes of 0.756 *M* calcium hypochlorite. Ordinates, logarithm of initial to remaining concentration of hypochlorite. Plot A (full line), observed data; plot B, (broken line) calculated for initial rapid reaction.

per anhydroglucose unit, and a second reaction proceeding at about one-tenth the speed. Although at pH 12 aqueous calcium hypochlorite was in equilibrium with about 0.5% of undissociated hypochlorous acid (5), the two reaction rates could not be attributed to the independent action of these two species of oxidant, because any disequilibrium between them would be redressed almost instantaneously. The assumption that the anhydroglucose units of starch underwent a rapid initial oxidation followed by a much slower secondary oxidation seemed more plausible, but failed to explain why about two-fifths of these units remained unoxidized at the end of the initial reaction (see below). The three-fifths that reacted therefore reduced an average of about 4 moles of hypochlorite per glucose residue, or enough to oxidize the whole of this portion to the level of oxalic and erythronic acids. A more detailed kinetic study of this oxidation, employing different concentrations and mole ratios of hypochlorite, would be desirable.

The conditions noted in Fig. 1 were used in subsequent oxidations, but when 3.0 moles of calcium hypochlorite per anhydroglucose unit had been utilized acetone was added to convert the excess hypochlorite to chloroform. The liquors from the oxidation contained no organic substances of interest, and the crude insoluble products, ranging in weight from 143 to 225% of the original starch, contained 20 to 31.3% of calcium. An attempt to remove this calcium as the oxalate yielded the information that much was already present in that form, and another attempt at removal as the alcohol-soluble chloride showed that most of the organic acids liberated were also soluble in 70 to 90% ethanol at  $-10^{\circ}$ .

Better results were obtained by adjusting an aqueous suspension of the calcium salts to pH 7 with dilute hydrochloric acid, removing those that failed to dissolve (fraction I, 37.5% by weight of the starch), and diluting the liquor with ethanol. In this way, any calcium hydroxide was eliminated as the soluble chloride, and the remaining calcium salts of the sugar acids were precipitated (fraction II, 87%). Calculations from the extensive analytical data showed that the free sugar acids from fraction I amounted to 22.5% of the starch, and those from fraction II to 62.5%; a further 3.7% was recovered as carbon dioxide present as calcium carbonate in the two fractions, but some or all of this amount might have been acquired adventitiously. Although hydrolyzates of the two fractions gave no chromatographic evidence of pentose sugars, the original sugar

acids yielded 0.73% and 2.34%, respectively, of furfural. These amounts were therefore attributed to the presence of 3.5% and 11.9% of uronic anhydride (6). After inorganic carbon dioxide had been removed, the conventional uronic anhydride determination gave the values 6.9% and 17.4%, respectively. These values were rejected as being too high, because Daniels (7) recently showed that only a small proportion of the "uronic anhydride" carbon dioxide yielded by a hypochlorite oxycellulose-6-C<sup>14</sup> originated from position 6, and that the determination could not be interpreted in such cases.

Preliminary experiments on the hydrolysis of the major fraction II with boiling *N* sulphuric acid showed that its copper-reducing power as glucose, originally 2.8%, increased to a nearly constant value of 46.4% within 3 hours; the carbon dioxide evolved in the same time corresponded to the destruction of 13% of "uronic anhydride". The latter observation suggested that the low final reduction reflected the presence of non-reducing constituents rather than that of acid-resistant aldobiuronic acids. After inorganic ions had been removed, the hydrolyzate was chromatographed with *n*-butanol - formic acid - water both on paper and on a cellulose column. The major fractions yielded four acidic compounds, of which three had the flow rates of glyoxylic, erythronic, and optically active tartaric acid. The column when subsequently eluted with water yielded 46% of a partly crystalline syrup consisting almost entirely of glucose, which was thoroughly identified. Even when the glucose was removed by a prior fermentation with yeast, the acidic products could not be obtained in a crystalline condition.

Khym and Doherty (8), however, separated glucuronic and galacturonic acids by adsorption on a column of anion-exchange resin followed by elution with 0.15 *M* acetic acid, the order of elution depending on the relative dissociation constants of the acids and the eluent. After preliminary experiments, the hydrolyzed acids from fraction II, freed from calcium and sulphate ions, were adsorbed on the anion-exchange resin, which failed to absorb the glucose. The column was then eluted exhaustively and in succession with 2 *N* acetic acid, *N* formic acid, and 0.5 *N* trifluoroacetic acid, the effluent being collected in 20-ml or 25-ml volumes which were examined by paper chromatography (Table I).

Although erythronic acid and erythroneolactone were removed simultaneously from the column by 2 *N* acetic acid, they had different  $R_F$  values when chromatographed on paper; both were isolated as the crystalline lactone. Glucuronic acid, however, chromatographed on paper as a single chemical individual. As expected, crystalline glyoxylic acid, mesotartaric acid, and DL-tartaric acid were recovered in the order of their dissociation constants, reported as  $10^4 K = 4.74, 6.3, \text{ and } 9.7$ , respectively (9, 10, 11). DL- and D-Tartaric acids had the same dissociation constant, and were therefore isolated from the ion-exchange column together; they were subsequently separated by fractional crystallization from water, in which the latter was about seven times more soluble than the former (12). Both were obtained with their correct melting points, the first being optically inactive and the second having its correct specific rotation of  $-14^\circ$  in water ( $c, 5.5\%$ ). The racemic acid was probably not an artifact, because an authentic sample of L-tartaric acid underwent no change in rotation when kept for 3 days in water buffered to pH 12 (as in the oxidation of the starch), or when boiled for 2.5 hours in *N* sulphuric acid (as in the hydrolysis of the oxidized starch). Prolonged attempts to isolate tartronic acid in the crystalline form, or as a crystalline derivative, failed.

The water-insoluble calcium salts comprising fraction I of the oxidized starch were next examined. Extraction with aqueous acetic acid left a residue of crude calcium oxalate. After calcium and a small amount of chloride ions had been removed from the

TABLE I  
 Column chromatography of hydrolyzed fraction II<sup>a</sup>

Eluent fraction	<i>R<sub>F</sub></i> on paper <sup>b</sup>	Weight, g	Substance	Eluent fraction	<i>R<sub>F</sub></i> on paper <sup>b</sup>	Weight, g	Substance
Column eluent 2 <i>N</i> acetic acid				Column eluent <i>N</i> formic acid			
60-98	.04-.09 <sup>c,e</sup>	—	Glucose	1850-2175	.00* .05-.07* .38-.45*	0.47	—
151-225	.12-.17*	0.33	—				
226-340	.12-.17*	0.85	—				
341-375	.12-.15/ .72-.74/	0.43	—	2176-2375	.01-.03* .05-.31*	1.58	Mesotartaric
376-509	.23-.28* .40-.45* .58-.61*	4.83	Erythronic acid and lactone <sup>d</sup>	2376-2465	.00*	0.18	—
510-525	.01-.13/ .23-.28* .40-.45/	0.04	—	2466-2650	.10-.28*	1.27	DL-Tartaric D-Tartaric
526-880	.01-.13/ .14-.17*	0.78	—	2651-3125	.00* .02-.04*	.35	—
881-1150	.04-.07/	0.34	Glucuronic	Column eluent 0.5 <i>N</i> trifluoroacetic acid			
1151-1300	.64-.74*	0.09	—	3516-3594	.00-.22* .32-.39* .52-.61/ .81-.85*	1.16	Oxalic Tartronic
1301-1620	.07-.11* .66-.74*	1.00	Glyoxylic				
1621-1849		0.11	—	Total		12.3 g	

<sup>a</sup>From 50 g of fraction II after deashing. Column of Dowex 1-X-4 resin (acetate form).<sup>b</sup>*n*-Butanol-formic acid-water eluent and bromophenol blue spray.<sup>c</sup>o-Aminodiphenyl spray.<sup>d</sup>Acid *R<sub>F</sub>*, 0.23-0.28; lactone *R<sub>F</sub>*, 0.40-0.45.<sup>e</sup>Faint spot.<sup>f</sup>Medium-sized spot.<sup>g</sup>Large intense spot.

extract, evaporation left 13.6% of fraction I as a colorless glass containing the free sugar acids. Hydrolysis of the acids followed by paper chromatography revealed the presence of glucose and glyoxylic acid, together with non-reducing compounds with *R<sub>F</sub>* values close to those of mesotartaric, L-tartaric, D-erythronic, and tartronic acids and of D-erythronolactone. The crude mixture amounted to only 5.1% of the starch, and was not separated quantitatively.

In Fig. 2, the total molar yield of each product was given the first time the substance was recorded; these yields were minimum estimates, with the exception of those for carbonic and tartronic acids, whose authenticity was doubtful. Together with the carbonic acid lost by decarboxylation during hydrolysis, they accounted for between 70 and 80% of the hypochlorite used in the oxidation. Only oxalic acid, and perhaps carbonic acid, occurred as such among the original, unhydrolyzed products, about 80% of which dialyzed through cellophane in aqueous solution and were therefore of no great molecular size. Nevertheless, paper chromatograms failed to reveal erythronic acid and lactone, glyoxylic, tartronic, and the tartaric acids in circumstances where their mobilities would have rendered them readily detectable. Since any ester groups would not have survived the alkalinity of the oxidation, the conclusion seemed inevitable that the acids remained attached to adjacent units of the oxystarch structure by glucosidic or acetal bonds until liberated by acid hydrolysis. Any speculation concerning the course of the oxidation had to take account of this circumstance.



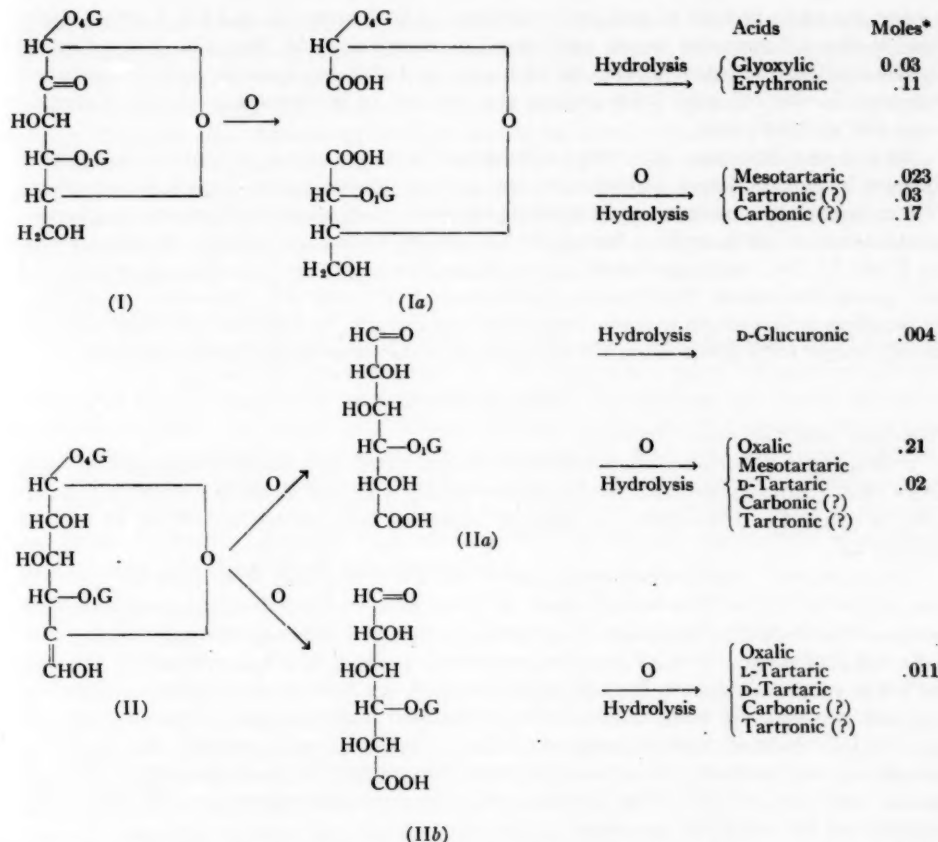


FIG. 2. Identified end products and postulated intermediates in oxidation of starch with calcium hypochlorite at pH 12. Adjacent anhydroglucose units, linked through fourth and first positions, denoted as  $_4\text{G}$  and  $_1\text{G}$ , respectively.

The relatively large yields of D-erythronic acid and lactone were readily explained by oxidation of an anhydroglucose unit in starch to the 2-keto structure I, followed by oxidative cleavage between the second and third positions to Ia, as Whistler and his collaborators (4, 5) had already supposed. Further oxidation of Ia would readily yield the precursors of mesotartaric and of tartronic acid. The other probable site of initial oxidation was the primary or sixth position of the anhydroglucose unit. It appeared necessary to assume that the enolic form of the 6-aldehyde structure II had at least a transitory existence, and yielded on further oxidation not only the D-glucuronic moiety IIa but also the L-iduronic derivative IIb, although only the former was isolated. Farley and Hixon (13) also isolated a small amount of glucuronic acid from a starch oxidized with 4 equivalents of bromine in neutral solution. By analogy with the easy cleavage of methyl- $\alpha$ -D-galactopyranuronoside and of pectic acid to free galacturonic acid by alkaline hypochlorite (14), the present oxidation at position 6 would lead to the collapse

\* Per anhydroglucose unit in starch.



of the glycosidic linkage at position 1, as shown in structures IIa and IIb. Further oxidation in the 2,3-positions would yield more mesotartaric acid from IIa, but L-tartaric acid from IIb, the other product in each case probably being oxalic acid. If oxidation occurred in the 1,2- and 5,6-positions, the product in both cases would be D-tartaric acid and carbonic acid.

Höning and Ruziczka (15), who oxidized starch with barium hypobromite in 0.02 *N* barium hydroxide, found maltobionic, and perhaps gluconic acid, among the products. These two substances were not detected on the present occasion. Neither were saccharinic acids, which might have been formed by the action of alkali on reducing structures such as I and II (16). D-Glucaric acid (saccharic acid) was not found, although mucic acid was prominent among the oxidation products of pectic acid (14); there was no evidence of 5-carbon acids such as arabonic and trihydroxyglutaric. At least some of these negative results might have arisen from the limitations of the experimental methods used.

### EXPERIMENTAL

#### *Materials and Analytical Methods*

Unless stated otherwise, all liquors were concentrated in a rotary evaporator at little more than room temperature, and analyses quoted were the mean of concordant duplicate or triplicate determinations. Specific rotations referred to the *D*-line of sodium and to 20°.

The commercial, unbleached wheat starch was simultaneously freed from fat and ash, and converted to the thin-boiling state, by being steeped for 5 days in changes of 97% acetic acid at room temperature (17). Periodate oxystarch, when reoxidized with bromine (18) and hydrolyzed, yielded brucine D-erythronate from which a solution of the free acid was prepared via the barium salt. Provided the brucine and barium salts were carefully purified, the D-erythronolactone crystallized when the solution was evaporated and the last traces of moisture were removed by distillation with toluene. Recrystallization from ethyl acetate yielded material with the correct (19) melting point, 102°, and specific rotation, -72.8°. This lactone, and also crystalline glyoxylic acid (20), were synthesized for reference purposes.

Solutions of reagent grade calcium hypochlorite were filtered through sintered glass and were standardized iodometrically or by the arsenite method. A blank, determined as 0.118 *M* by both methods, remained unchanged in titer for at least 44 hours at 20°, and conversion to chlorate was therefore negligible (5). The calcium content of the oxystarch was determined either as carbonate by incineration to constant weight at 475° to 525°, or as sulphate by incineration at 900° after treatment with sulphuric acid; precipitation as the oxalate and titration of the latter with 0.1 *N* potassium permanganate in dilute sulphuric acid (21) was also used. To determine inorganic chloride, an aqueous solution or suspension of the sample was acidified with pure, 6% nitric acid and was titrated potentiometrically with 0.1 *N* silver nitrate to an end point at 275 millivolts (22). Inorganic carbonate was estimated by decomposing a 1- to 2-g sample with 12% hydrochloric acid at 70° in an uronic acid apparatus (23) and weighing the carbon dioxide evolved; uronic anhydride carbon dioxide was then determined separately by boiling a similar still residue under reflux for 3 and 5 hours and extrapolating the data to zero time. Somogyi's method (24) was used to determine copper-reducing power, the reagents being standardized with pure glucose.

Salts were usually converted to the free acids by passing the aqueous solution through a column of the cation-exchange resin, "Amberlite IR-120", which was subsequently

eluted with water until the effluent became neutral. Aliquots of the effluents could then be examined by descending paper chromatography, the eluent being the organic phase of a water - *n*-butanol - 85% formic acid mixture (385:500:115) equilibrated by boiling under reflux for 1 hour (25). Since bromphenol blue in 95% ethanol (26) was almost always the spray, the chromatograms first had to be dried *in vacuo* at 110° for 8 hours to eliminate the last traces of formic acid. The other acids then gave well-defined yellow spots on a blue background. An acidic solution of *o*-aminodiphenyl (27) gave brown, purple, and yellow spots with glucose, D-glucuronic acid and its lactone, and with glyoxylic acid, respectively, while a spray of alkaline hydroxylamine followed by ferric chloride in 1% hydrochloric acid (28) gave clear brown spots with lactones.

#### Rate of Oxidation (Fig. 1)

The starch, 2.50 g with 10.7% moisture (13.7 mmoles), was dispersed in 12.5 ml of water and the mixture was gelatinized by the addition of 37.5 ml of boiling water. After immersion in a boiling water bath for 10 minutes, the solution was cooled to room temperature (20°), and mixed with 125 ml of water containing 75.6 mmoles of calcium hypochlorite and 1 g of powdered calcium hydroxide. The flask used was protected from light, the mixture was mechanically stirred, and the hydrogen ion concentration was kept at all times within the limits pH 12.1 to 11.6 by the addition of two 1-g portions of calcium hydroxide. Aliquots were removed at intervals and the amount of residual hypochlorite was determined iodometrically.

#### Larger-Scale Oxidation

A 225-g sample of the starch (7.2% moisture) was dissolved in 5 liters of water in the way described, and was oxidized with 10 liters of calcium hypochlorite kept near 20°. The concentrations of the starch per  $C_6H_{10}O_5$  unit and of hypochlorite were 86 mmoles and 443 mmoles per liter, respectively. A total of 210 g of powdered calcium hydroxide was added during the oxidation to maintain the alkalinity between pH 11.8 and 12.1. After 2.98 moles of hypochlorite per anhydrohexose unit had been consumed, the reaction was stopped by the addition of 500 ml of acetone. The mixture was filtered and the insoluble material was repulped in 1000 ml of water.

The combined liquors were neutralized with carbon dioxide, the precipitated calcium carbonate was discarded, and the concentrated mother liquor was diluted with much ethanol. Crystalline calcium acetate monohydrate (from the acetone), contaminated with the chloride and carbonate, separated, but no salt derived from the oxidized starch could be found.

A slurry of the above, insoluble calcium salts in 2000 ml of fresh water was then neutralized to pH 7.0 by adding 300 ml of concentrated hydrochloric acid, neutralization being considered complete after the pH remained unchanged for 24 hours. The insoluble residue was recovered, slurried with 1000 ml of water in a Waring Blendor to reduce the particle size, extracted twice more with a total of 1100 ml of water, and dried in the air. Yield of fraction I, 78.2 g or 37.5% by weight of starch. All the neutral filtrates and washings from fraction I were combined, concentrated to 700 ml, and diluted with 2 volumes of ethanol to precipitate the water-soluble calcium salts of the oxystarch. This precipitation was repeated twice more to remove calcium chloride, and the product was dried in the air. All alcoholic liquors were combined, concentrated, and again diluted with ethanol to recover another 14 g of calcium salts. These salts were combined with the main crop to give 181.7 g (87%) of fraction II.

Found for fraction I: ash at 1200° (CaO), 32.4; Cl, 0.23; moisture, 8.1; furfural, 0.73;

uronic anhydride, 6.9; inorganic  $\text{CO}_2$ , 5.5%. Samples, 0.139 g, 0.204 g, and 0.200 g, reduced 9.7 ml, 14.2 ml, and 14.1 ml, respectively, of acid potassium permanganate, the corresponding oxidation equivalent being 51.3, 51.3, and 51.9% of calcium oxalate monohydrate. When corrected for calcium chloride, calcium carbonate, and moisture, the calcium content of the product was 22.9%, giving a yield of 60.1% of fraction I (22.5% of the starch) as sugar acids of average equivalent weight 68.3.

Found for fraction II: ash (as  $\text{CaSO}_4$ ), 37.3; Cl, 1.45; moisture, 11.9; furfural, 2.34; uronic anhydride, 17.3; inorganic  $\text{CO}_2$ , 1.84%. Correction for calcium carbonate, calcium chloride, and moisture gave Ca, 10.4% for the salts of the sugar acids, whose equivalent weight was 173 and whose yield was 73.6% of fraction II or 64% of the starch.

A solution of fraction II (2 g) in 15 ml of water was freed of cations and the effluent was diluted to 100 ml. One 20-ml aliquot of this acidic effluent, corresponding to 0.4 g of fraction II, yielded 0.282 g, or 70.5%, of sugar acids when dried *in vacuo* to constant weight. Two other aliquots were mixed with 0.1 *N* sodium hydroxide and were back-titrated after 16 hours to a phenolphthalein end point with 0.1 *N* hydrochloric acid; the aliquots neutralized 4.46, 4.52 milliequivalents per gram. Since 1 g of fraction II originally contained 0.41 milliequivalent of chloride, the value for the sugar acids was 4.08, corresponding to a neutralization equivalent of 705/4.08 or 173. Both this value and the yield were in good agreement with those calculated from the analytical data.

A 1.32-g sample of fraction II was freed from cations and the solution was dialyzed through collodion against two 4-liter volumes of 0.01 *N* hydrochloric acid for 36 hours, then against the same volumes of distilled water to remove the hydrochloric acid. Evaporation of the residual liquor yielded 0.153 g or 11.6% of non-dialyzable material, corresponding to 16% of the free sugar acids.

#### *Products from Hydrolysis of Fraction II*

A solution of fraction II, 0.598 g, in 20 ml of *N* sulphuric acid was boiled under reflux, aliquots being periodically removed and neutralized with sodium hydroxide. After 0, 0.25, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.6, and 8.6 hours the copper reduction as glucose (24) was 2.8, 11.0, 17.8, 26.0, 33.5, 35.9, 37.0, 38.7, 41.2, and 42%, respectively. Hydrolysis for 2.5 hours was judged sufficient in the subsequent work. A mixture of fraction II, 1.02 g, and 60 ml of *N* sulphuric acid, contained in the uronic acid apparatus (22), was freed from inorganic carbon dioxide by the passage of nitrogen for 1 hour, and was then boiled under reflux for 2.5 hours. Found: uronic anhydride, 9.4%, corresponding to the decomposition during hydrolysis of 13.1% of carboxyl groups in the sugar acids.

An aqueous solution of the fraction II from an earlier oxidation, 2 g, was decationized, evaporated almost to dryness, and redissolved in 40 ml of *N* sulphuric acid. After hydrolysis as just described, sulphate ion was precipitated by the exact amount of aqueous barium hydroxide, and the filtrate on evaporation yielded 1.86 g of a syrup. This syrup, 1.58 g, was chromatographed on a cellulose column. All acidic material was removed by the passage of 5500 ml of the butanol-formic acid-water mixture, and then the glucose was eluted with 5000 ml of water. Evaporation of the aqueous effluents left 0.675 g of a syrup (43% of the calcium-free material) which partly crystallized when stored *in vacuo* over solid sodium hydroxide. The phenylosazone (29) decomposed at 198–199°, or in the proper range for the glucose derivative. The corresponding osotriazole (30) had the melting point 195.5°, not depressed by admixture with authentic glucose phenylosotriazole, m.p. 195°.

Fifty grams of fraction II, suspended in water and mixed with 70 g of "Amberlite

IR-120", was put on the top of a column of the same resin and eluted with water. Evaporation of the effluent left 51 g of calcium-free, acidic syrup which was hydrolyzed, the hydrolyzate then being freed from sulphate ion by the addition of the exact amount of aqueous barium hydroxide. The filtrate and washings were concentrated to 1500 ml and passed through a 25 cm  $\times$  3.5 cm column containing "Dowex 1-X-4" anion-exchange resin (free base) at a rate of 17 ml per minute. Paper chromatography of the effluent revealed no evidence of any sugar save glucose, and epimerization to other sugars had not occurred during the 90-minute exposure to the strongly basic resin (31). The resin with its adsorbed sugar acids, but no more than traces of glucose, was transferred without delay to the top of a 100  $\times$  5.6 cm column containing the same resin in its acetate form. Elution of the column at once began with 2 *N* acetic acid at a flow rate of 1.5 ml to 3 ml per minute, and the effluent was collected in 25-ml or 20-ml fractions. Every 20th or 30th fraction was evaporated to 0.3 ml, and chromatographed on paper. When nothing more was extracted by the acetic acid, the eluent was changed to *N* formic acid, which was later replaced by 0.5 *N* trifluoroacetic acid, the total volume of effluents being more than 60 liters. Fractions shown by paper chromatography to contain the same compound or compounds were combined and concentrated to syrups. Of these syrups, those derived from the following sets of fractions (Table I) were examined.

#### Fractions 226-340

The corresponding syrup, 0.85 g, yielded several spots, revealed by the bromphenol blue spray, when chromatographed on paper for several days. When a solution was titrated with alkali to pH 7, the behavior was that of a lactone. Several attempts to obtain a crystalline acid or calcium salt from the syrup failed.

#### D-Erythronolactone

Fractions 376-510 yielded 4.83 g of a syrup which crystallized when nucleated with 2 mg of pure D-erythronolactone; 1.2 g of crystals melting at 85-95° separated. Recrystallization yielded 1 g of material whose neutralization equivalent, 117.4, melting point, 101-103°, and specific rotation,  $-72.9^\circ$  (*c*, 4.57, water) agreed with accepted values (19, 32). A mixed melting point with an authentic sample was undepressed and the infrared spectra of both samples were identical.

#### D-Glucuronic Acid

The syrup, 0.322 g, from fractions 924-1105 was adsorbed on a microcolumn of "Dowex 1-X-4" anion-exchange resin (free base form), which was quickly eluted with water to remove any cations. Elution with 2 *N* acetic acid began immediately, and evaporation of the first 85 ml yielded 0.249 g of a syrup. Nucleation of this syrup with 0.3 mg of D-glucuronic acid caused the crystallization of 0.106 g of the crude material, which was isolated by pressing the partly crystalline mass between pads of filter paper. The material recovered from the paper was heated to convert it to the lactone, but the product could not be crystallized. The glucuronic acid, after recrystallization from aqueous ethanol, melted correctly at 154-155° and had the correct (33) equilibrium specific rotation in water,  $+35.6^\circ$  (*c*, 2). The infrared spectrum was identical with that of pure D-glucuronic acid prepared from the crystalline lactone.

#### Glyoxylic Acid

Fractions 1301-1500 yielded 0.917 g of a syrup which when chromatographed on paper gave a yellow spot, *R<sub>F</sub>* 0.61-0.70, with the *o*-aminodiphenyl spray, and a spot of *R<sub>F</sub>* 0.66-0.74, with bromphenol blue. The behavior of authentic glyoxylic acid was



identical. The syrup gave 59% of the theoretical yield of yellow, crystalline, glyoxylic acid 2,4-dinitrophenylhydrazone melting with decomposition at 189–191°, in agreement with the recorded (4) value. Found: N, 22.1. Calc. for  $C_8H_6N_4O_6$ : N, 22.1%.

#### *Mesotartaric Acid*

The syrup, 1.226 g, from fractions 2176–2300 partly crystallized when nucleated with 0.3 mg of mesotartaric acid, and its  $R_F$  value, 0.61–0.70, when chromatographed on paper was identical with that observed for an authentic sample. This mobility was 0.78–0.85 of that possessed by authentic L-tartaric acid. Some of this syrup, 0.41 g, was neutralized to pH 8 with 0.345 N barium hydroxide, and 0.40 g of a crystalline barium salt separated. Found (after purification): Ba, 63.1%. Calc. for  $BaC_4H_4O_6 \cdot H_2O$ : Ba, 65.1; for  $BaC_4H_4O_6 \cdot 2H_2O$ : Ba, 61.1%.

A portion, 0.206 g, of the above salt when deionized gave 0.100 g of the crystalline free acid which melted at 130–137°. These crystals were neutralized to pH 3.5 with 0.25 N potassium hydroxide; dilution of the liquor with 2 volumes of ethanol and the addition of 0.3 mg of monopotassium mesotartrate caused the crystallization of that substance. Yield, 0.082 g after purification by extraction with ethanol. Found: ash as carbonate, 36.5%. Calc. for  $KC_4H_5O_6$ :  $K_2CO_3$ , 36.7%. Upon recovery from this salt, the colorless crystals of the free acid were optically inactive and had the melting point, 139–140°, reported for pure mesotartaric acid (34).

#### *DL- and D-Tartaric Acid*

Fractions 2466–2600 yielded a mixture, of which 0.612 g crystallized and 0.48 g remained as syrup. After recrystallization from acetone, the crystals melted at 203–204° and their neutralization equivalent of 76.1 was close to that, 75, calculated for a tartaric acid. A 0.315-g sample of these crystals yielded 0.298 g of the white monopotassium salt which was then twice recrystallized from water. Found: ash as carbonate, 36.7%. Calc. for  $KC_4H_5O_6$ :  $K_2CO_3$ , 36.7%.

A part of this salt, 0.14 g, yielded 0.11 g of crystalline free acid melting with decomposition at 204° after recrystallization from tetrahydrofuran. The melting point of DL-tartaric acid was 204–206° (35). As expected, the crystals were optically inactive and yielded a precipitate when an aqueous solution was diluted with a saturated aqueous solution of calcium sulphate. This test distinguished the racemic from the optically active forms of tartaric acid (36). The paper chromatographic flow rate of an aqueous solution of the crystals (Table I) was identical with that of authentic DL-tartaric acid, which was a streak of  $R_F$  0.32–0.62 with reference to L-tartaric acid as standard.

Most of the syrup from the original crystallization, 0.41 g, was freed of any contaminating cations, and was converted as above to the monopotassium salt, a solution of which in 66% ethanol was seeded with a trace of monopotassium D-tartrate. The crystals which separated after 24 hours near 0°, 0.30 g, were washed in ethanol and twice recrystallized from hot water. Yield 0.29 g. Found: ash as carbonate, 36.9%. Calc. for  $KC_4H_5O_6$ :  $K_2CO_3$ , 36.7%. When a solution of this purified salt was freed from cations, the acidic effluent crystallized solidly; melting point, 168–170°, and specific rotation in water  $-14.0 \pm 0.6^\circ$  ( $c$ , 5.5). The melting point reported (35) for D-tartaric acid was 170°, and the specific rotation for  $c$ , 5.5, was calculated from Landolt's formula (37) as  $-14.3^\circ$ . When chromatographed on paper, the flow rate of an aqueous solution of the crystals was identical with that of authentic L-tartaric acid.

*Fractions 3516-3553*

These fractions were evaporated to 15 ml, diluted with water, and evaporated several times to expel most of the trifluoroacetic acid. Continuous extraction of the final aqueous residue for a total of 17 hours with ether yielded 1.16 g of syrup, the first portion of which, 0.93 g, partly crystallized during isolation. An aqueous solution of these crystals, 0.21 g, was decolorized with absorbent carbon and was then evaporated over solid sodium hydroxide at 30-mm pressure. A control experiment showed that oxalic acid dihydrate was stable under these conditions, but became anhydrous when drying agents more powerful than sodium hydroxide were used. The residual, transparent crystals after recrystallization from hot water had the melting point, 100–101°, of oxalic acid dihydrate. A mixed melting point with an authentic sample was not depressed. A 16-mg sample reduced 9.74 ml of 0.026 *N* potassium permanganate, the value calculated for oxalic acid dihydrate being 9.73 ml.

The ether extract from which the oxalic acid had originally crystallized yielded 0.71 g of a syrup, 0.2 g of which was freed of any cations. When the concentrated, acidic effluent was neutralized with 0.044 *M* calcium hydroxide about 15 mg of calcium oxalate separated and was removed. Dilution of the concentrated filtrate with 2 volumes of ethanol precipitated 0.155 g of a calcium salt (A) and evaporation of the mother liquor yielded a further 0.087 g (B). Calcium salts (A) and (B) were separately freed from calcium ions and the acidic effluents were chromatographed on paper. At low concentrations the  $R_F$  values for authentic tartronic acid, acids A and B, were 0.30–0.34, 0.27–0.31, and 0.32–0.34, respectively; at higher concentrations the values were 0.30–0.47, 0.40–0.48, and 0.40–0.47. The similar variations in  $R_F$  with concentration made it probable, but failed to prove, that acids A and B consisted of tartronic acid. Acid A was adsorbed on a micro "Dowex-1-X-4" anion-exchange column, which was then eluted with *N* acetic acid before the product was recovered in 25% aqueous formic acid. The syrup from the effluent, however, failed to crystallize, either as such or when converted to the neutral potassium or calcium salts. Control experiments with authentic, crystalline tartronic acid showed that it was eluted readily from the above resin with formic acid, and readily yielded a crystalline potassium salt and a precipitate of calcium salt.

*Examination of Fraction I*

Five grams of the original, water-insoluble calcium salts was mechanically agitated for several hours in an excess of aqueous 5% acetic acid. The undissolved portion was re-extracted in the same way, was washed with water, and was dried. Yield 3.1 g or 62%. Found: ash as sulphate, 77.9%; or Ca, 22.9%. Calc. for  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ : Ca, 27.4%. A solution of this product in 40 ml of 20% hydrochloric acid was continuously extracted with ether for 14 hours, and evaporation of the extracts yielded 2.15 g of crude oxalic acid. Recrystallization from a little hot water left 2.08 g of the pure substance with the correct permanganate equivalent. The yield corresponded to 48.2% of calcium oxalate monohydrate in fraction I.

An acetic acid extract from another 5 g of fraction I was freed by an ion-exchange resin from calcium ions, and then from chloride ions by shaking with a slight excess of silver carbonate, the final filtrate being concentrated to dryness. A brittle glass remained; weight 0.67 g (5.1% of the starch) of which 69% passed through a cellophane membrane when dialyzed against water. A part of this glass was hydrolyzed and the sulphuric acid was precipitated as the barium salt. The filtrate when chromatographed on paper



yielded spots with  $R_f$  values corresponding to the substances noted in Table I, those for D-glucose, D-erythronic acid, and D-tartaric acid being most intense.

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## PHOTOOXIDATION OF AZOMETHANE

### IV. THE ROLE OF FORMALDEHYDE<sup>1</sup>

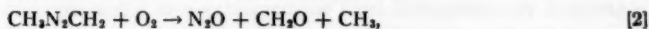
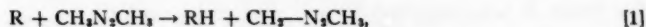
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#### ABSTRACT

The photooxidation of azomethane has been reinvestigated over a range of conversion extending to at least 7% at relatively high oxygen pressure and at 162° C. Kinetic and tracer (added C<sup>13</sup>H<sub>2</sub>O) studies support the view that the formaldehyde formed in the reaction can act as a source of the oxides of carbon. These were found to be enriched in C<sup>13</sup> in the tracer work.

#### INTRODUCTION

One of the puzzling features of the mechanism of the photooxidation of azomethane (1) has been the nature of the product responsible for the self-inhibition (2, 3) of the reaction. Formaldehyde, nitrous oxide, and "excess nitrogen" (3) are produced at rates which decrease with the time of exposure. These products are thought (1, 3) to arise via the reactions



where R is some radical in the system and [2] and [3] are written as over-all processes which might occur in stages. Provided methyl and methoxyl, or radical products of their reaction with oxygen, can function as R in [1], the elements of a chain reaction are present in the mechanism as appears to be required by the data (3).

It was recognized (2, 3) that when this chain was inhibited by some product, the inhibition mechanism must involve the production of carbon monoxide and, probably, of carbon dioxide. The mechanism suggested was a competition for the radicals R by the inhibiting substance, here designated by R'H.



It is postulated that the "other products" do not propagate chains to any extent. Initially it was suggested that formaldehyde should be identified as R'H (2). While this suggestion led to a satisfactory qualitative explanation of the phenomenon, it was not compatible with later (3) quantitative data. Therefore another mechanism, which identified R'H with performic acid, was advanced.

The purpose of the present work was to obtain data confirming, or otherwise, the hypothesis that formaldehyde could not function as R'H. In addition to a purely kinetic approach, experiments were done in which formaldehyde-C<sup>13</sup> was added to the reaction system. From a kinetic point of view the concentration of formaldehyde found at the end of an experiment, including that formed in the reaction, is indicative of whether or not formaldehyde was consumed in the reaction. If such consumption did indeed

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occur, and if the mechanism of the consumption involves the inhibition mechanism [4], [5], and [6], the oxides of carbon found should be enriched in  $C^{13}$ .

## EXPERIMENTAL

### *Apparatus*

The vacuum apparatus, thermostatted air oven, and optical arrangements were essentially those used in an earlier investigation (3) with only minor modifications. The volume of the 5-cm diameter reaction cell was 180 cc, that of the complete reaction system, including the stirrer, 256 cc. All connecting tubing through which formaldehyde was required to pass could be heated to 140° C to prevent polymerization of that substance.

### *Materials*

Azomethane (Merck of Canada, Montreal) was purified in the vacuum system in the usual manner (1, 2, 3). Gas chromatographic separation and estimation along with mass spectrometric identification of impurities revealed the presence in this sample of trimethyl hydrazine (<2%), methyl chloride (<0.1%), and methanol (<0.1%). The latter impurity was particularly objectionable in the experiments done at low conversions and, for these, it was removed by gas chromatography.

Oxygen was prepared by heating potassium permanganate and was separated from condensable impurities by passage through a trap at -196° C.

Formaldehyde- $C^{13}$  ( $C^{13}/C^{12} = 20.4\%$ ) was obtained as required by heating a sample of enriched  $\alpha$ -polyoxymethylene supplied by Dr. L. C. Leitch of these laboratories.

The trisodium salt of chromatropic acid (4,5-dihydroxy-2,7-naphthalene disulphonic acid, trisodium salt) used in the analysis of formaldehyde was prepared by titration of an aqueous solution (15%) of chromatropic acid disodium salt (Eastman Kodak) with a solution of sodium hydroxide (3%) to pH 7 as measured on a pH-meter. The salt was purified by fractional precipitation (3) and the beige-colored crystals were kept in dark bottles.

### *Procedure*

Aside from minor details most operations in an experiment were done as described previously (3).

For the experiments with added formaldehyde- $C^{13}$ , several break-seal bulbs, whose volumes were known, were filled from a manifold at one time using the filling technique developed earlier (3). The formaldehyde content of one bulb was determined and that of each of the others was calculated from the known volumes. Mixtures of azomethane, formaldehyde, and oxygen were prepared in the reaction system as described before (3).

### *Analysis of Products*

After an exposure the products were condensed at -196° C in a U tube and the noncondensable gases ( $O_2$ ,  $N_2$ ,  $CO$ ) were collected and analyzed over a hot mixture of copper and cupric oxide (1). Carbon dioxide and nitrous oxide were separated from a Le Roy still (4) at -160° C and analyzed by mass spectrometry. Small quantities of formaldehyde, methyl chloride (present as an impurity), and azomethane always appeared in this fraction and prevented accurate estimation of the major components. Some uncertainty is also introduced into the  $C^{13}/C^{12}$  ratio of the carbon dioxide because of the effects of these impurities.

Formaldehyde was separated from the remaining liquid products by a single passage through a Le Roy still held at  $-130^{\circ}\text{C}$  and condensed onto a frozen solution of the trisodium salt of chromatropic acid held at  $-196^{\circ}\text{C}$ . All connecting tubing accessible to the formaldehyde vapor was held at  $140^{\circ}\text{C}$ . Procedures developed earlier (3) were followed in detail for the remaining steps in this modification of the chromatropic acid method (5). The liquid products were collected and analyzed for methanol by gas chromatography in a column developed by Blake and Kutschke (6) (25% dinonyl phthalate and 5% glycerol on Fischer Columapak;  $29^{\circ}\text{C}$ ;  $\text{H}_2$  flow rate, 45 cc/min). Peak areas were compared with those of standard samples.

## RESULTS

Table I gives the data from several experiments at  $162^{\circ}\text{C}$ . The conditions were maintained as closely as possible to the earlier work (3). Oxygen concentration was sufficiently high to suppress completely the formation of methane and ethane. The trend of the

TABLE I  
Yields of products in the photooxidation  
( $p_{\text{azo}} = 57$  mm,  $p_{\text{O}_2} = 7$  mm at  $0^{\circ}\text{C}$ ; reaction temperature,  $162^{\circ}\text{C}$ ;  
 $I_a = 4.0 \times 10^{-12}$  quanta/cc sec)

Time, minutes	$\mu\text{moles}$					
	$\text{N}_2$	CO	$\text{CO}_2$	$\text{N}_2\text{O}$	$\text{CH}_2\text{O}$	$\text{CH}_3\text{OH}$
1	—	—	—	—	—	0.8
2.5	—	—	—	—	—	1.4
4	—	—	—	—	—	2.2
5	5.0	1.33	0.7	2.1	2.8	4.0
5	5.2	1.15	—	—	2.4	—
15	12.7	5.10	1.6	4.4	3.9	12.5
15	13.5	5.04	—	—	4.2	12.4
25	21.7	8.90	2.2	5.0	5.3	22.4
35	30.4	12.2	3.7	7.5	4.9	33.4
45	42.1	17.5	4.9	7.0	5.7	41.9
45	39.7	17.0	4.5	6.8	—	42.3
55	46.8	20.8	5.2	7.7	5.8	48.8
20	14.17	Oxygen absent				
40	28.50	Oxygen absent				

yields with time is shown in Fig. 1 in which quantum yields of a product, defined as the ratio of the amount of a product formed per unit time to that of nitrogen formed in the absence of oxygen with otherwise identical conditions, are plotted as a function of conversion. The latter corresponds to  $D_1$  of reference 2 and is calculated with the assumptions that (a) each molecule of azomethane which disappears gives rise to a molecule of nitrogen or of nitrous oxide, and that (b) the stirring was completely efficient. Aside from that of methanol and formaldehyde the general forms of the curves in Fig. 1 agree with those obtained earlier (2, 3).

Results from experiments with added formaldehyde- $\text{C}^{18}$  are given in Table II. The amount of formaldehyde added corresponded to a concentration about twice as great as that found after long experiments without added formaldehyde. Figure 2 shows that the concentration of formaldehyde rapidly adjusts to that same, approximately steady,

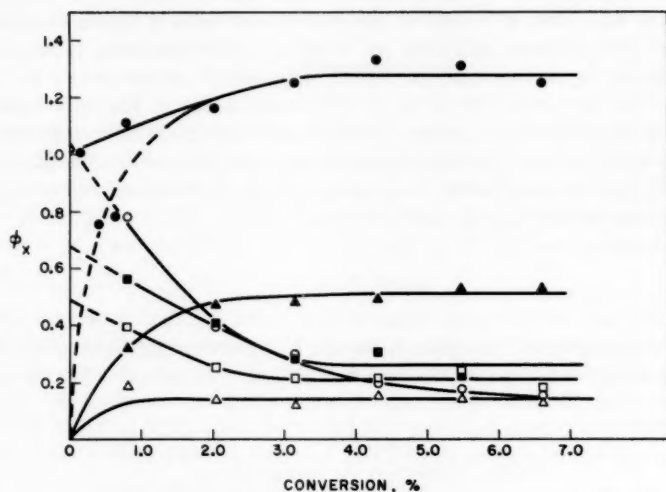


FIG. 1. Quantum yields as a function of conversion at 162°C: ● methanol, ○ formaldehyde, ■ nitrous oxide, □ secondary nitrogen, ▲ carbon monoxide, △ carbon dioxide.

TABLE II  
Yields of products in the photooxidation  
(Presence of 9.7  $\mu$ moles of formaldehyde- $C^{13}$ )

Time, minutes	$\mu$ moles			$100C^{13}/C^{12}$	
	$N_2$	CO	$CH_2O$	CO	$CO_2$
1	—	0.9	6.2	12	19
2	2.4	1.4	6.4	16	14
5	5.2	3.2	5.9	13	10
15	10.2	6.9	5.4	12	—
20	14.2	7.9	6.0	13	14

NOTE: Conditions as in Table I.

concentration and thereafter remains unchanged. The yields of carbon monoxide obtained from experiments of low conversion were much greater in the presence of added formaldehyde than in its absence. This is shown in Fig. 3 as a plot of the absolute amounts of carbon monoxide formed at various times for the two sets of conditions. The slope of the curve (Fig. 3, open circles) obtained in the presence of formaldehyde becomes constant at about the degree of conversion at which the formaldehyde concentration reaches its approximately steady value (Fig. 2).

The last two columns of Table II present the data on the isotopic composition of the oxides of carbon found. There is little doubt that these compounds are enriched in  $C^{13}$ . Mixtures of formaldehyde- $C^{13}$  and carbon monoxide were carried through the procedure of an experiment in the absence of ultraviolet illumination. On analysis no detectable enrichment was observed in the carbon monoxide.

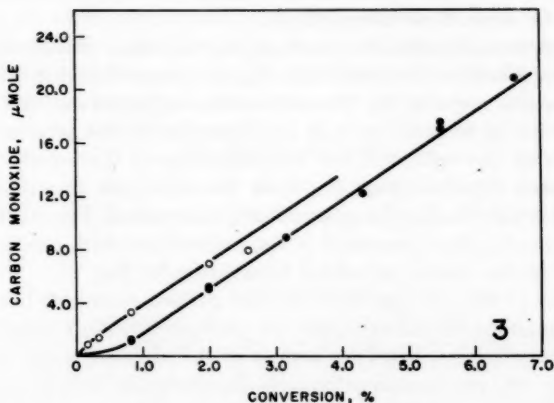
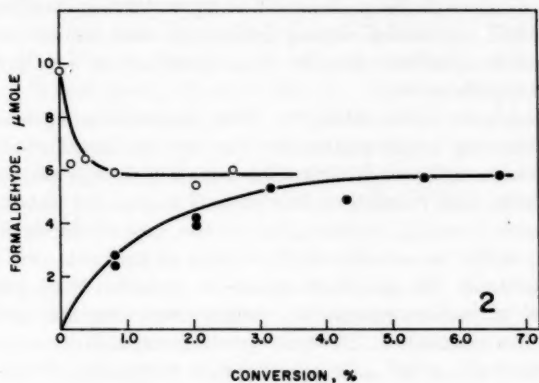


FIG. 2. Variation of the yield of formaldehyde with conversion: ● normal photooxidation, ○ 9.8  $\mu\text{moles}$  formaldehyde- $\text{C}^{13}$  added initially.

FIG. 3. Variation of the yield of carbon monoxide with conversion: ● normal photooxidation, ○ 9.8  $\mu\text{moles}$  formaldehyde- $\text{C}^{13}$  added initially.

#### DISCUSSION

This report is concerned only with the reaction at  $162^\circ\text{C}$  with conditions used in earlier investigations (1, 2, 3) and is confined largely to the discussion of the likelihood that formaldehyde can inhibit the reaction under these conditions. Moreover, the discussion is limited to the region of conversion greater than about 1%. At lower conversions, reproducible data are very difficult to obtain.

In an earlier communication (3) several arguments were offered to refute the hypothesis that formaldehyde could participate in the inhibition mechanism. These were of two types: kinetic, which discussed the shape of the yield vs. time curves, and isotopic, which involved the results of a photooxidation experiment done in the presence of formaldehyde enriched in oxygen-18.

In considering the kinetic arguments it must be borne in mind that, to a precision of about 10–15%, good agreement between this and the earlier study is found in the



yield vs. time curves of many of the products. This agreement is excellent in the curves for total nitrogen, carbon monoxide, nitrous oxide and, with somewhat less precision, for secondary nitrogen and carbon dioxide. Analogous curves for formaldehyde and methanol yields differ significantly.

The present data indicate quite definitely that formaldehyde concentration does indeed approach a stationary value with time. The earlier data, covering a somewhat smaller range of conversion, did not exhibit such a limit although the existence of such a limit is not incompatible with those data. For some reason as yet unknown the limiting concentration, or possible limiting concentration in the case of the earlier work, found in the two sets of data differ by a factor of about two as does the time (or conversion) required to attain that limit. The excellent agreement between the yields of other products, especially those of carbon monoxide, indicate that the two sets of data were taken under very similar conditions. The only possible explanations involve either an unknown systematic error in one or the other analytical techniques (which were virtually identical) or a difference in surface characteristics causing this specific effect. At present no choice is possible between these alternatives.

More extensive data are presented here concerning the effect of added formaldehyde on the yields of some products. In particular, Fig. 2 shows that formaldehyde is not inert in the system as was required by the mechanism suggested earlier (3).

That the consumption of formaldehyde is accompanied by the production of carbon monoxide is indicated by the enhanced rate of production of that product when excess formaldehyde is present initially (Fig. 3). After formaldehyde has been depleted to approximately its stationary value (i.e. about 0.5% conversion, Fig. 2), the yield-time curve for the formation of carbon monoxide is not inconsistent with a rate of production similar to that found in the absence of added formaldehyde (Fig. 3).

The  $C^{13}$  experiments (Table II) also indicate that carbon monoxide can be formed in this system from a formaldehyde intermediate. In addition it is clear that carbon dioxide also can arise from the same intermediate (values of the absolute yield of nitrous oxide and of carbon dioxide were not measured in these experiments). While these conclusions disagree with those reached on the basis of the  $O^{18}$  work reported earlier (3) the relative insensitivity of the present technique to errors caused by possible exchange over the hot copper oxide suggest that they are the more reliable. The value of the  $C^{13}/C^{12}$  ratio found in the oxides of carbon are lower than that of the added formaldehyde. This implies that some compound, presumably formaldehyde, which is produced in the system also acts as a precursor to the oxides of carbon.

It may be concluded from the present data that formaldehyde is not inert in this photooxidation system and that the oxides of carbon can be formed from the reactions of this compound.

If equations [5] and [6] represent the major sources of the oxides of carbon, then  $R_{CO}/R_{CO_2} = k_5/k_6$ . The data from 15 minutes to 55 minutes yield a value  $k_5/k_6 = 3.7 \pm 0.1$ , a value which is somewhat lower than that ( $\sim 5$ ) which can be deduced from similar data in the earlier work (3). A detailed mechanism has been suggested (7) for these reactions which involves the formation of  $HCO_3$  radicals followed by isomerization to  $O=COOH$  and decomposition either to carbon monoxide and  $HO_2$  radical or to carbon dioxide and an hydroxyl radical.

If, in addition to the assumption above, it is also valid to assume (a) that nitrous oxide and secondary nitrogen arise only from [2] and [3], and (b) that [2] and [3] represent the sole fates of  $CH_2N_2CH_3$  radicals formed in [1], and [5] and [6] the sole fates of formyl

radicals formed in [4], then it follows that  $(R_{CO} + R_{CO_2})[A] / \{(R_{N_2})_{secondary} + R_{N_2O}\}[F] = k_1/k_4$ . Calculations based on the data of Table I give  $k_1/k_4 = 212 \pm 10$  with no obvious trend with conversion. If  $A_1/A_4$  is taken as unity approximately, this calculation indicates that  $E_1 = E_4 = 4-5$  kcal/mole. Since it has not been established that the radical R in [1] and [4] is a single species (probably OH, HO<sub>2</sub>, CH<sub>3</sub>O, and CH<sub>3</sub>O<sub>2</sub> enter into these reactions at various rates), the value calculated cannot be ascribed to a single reaction. However, it might be noted that the difference obtained is relatively large compared with the difference  $E_1 - E_4$  when R is a methyl radical. This latter difference has been reported as 2.2 kcal/mole (8).

Brief mention should be made at this point of the shape of the curve of the quantum yield of methanol as a function of conversion (Fig. 1). Analytical uncertainties are rather large in the low-conversion region and rigorous attention had to be paid to the purity of the reactants. The combination of these two factors renders the determination of quantum yields in this region highly imprecise. On the basis of the present data it is impossible to decide whether  $\Phi_{CH_3OH}$  approaches unity or zero at these conversions (Fig. 1). While of obviously considerable significance, possible explanations of either extrapolation are closely associated with the mechanism of formation of methyl hydroperoxide recently found to be a product in this system (9). Detailed consideration of these points will be presented at a later time.

#### ACKNOWLEDGMENTS

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## THE PREPARATION AND SOME PROPERTIES OF GERMANIUM DIFLUORIDE<sup>1</sup>

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### ABSTRACT

Germanium difluoride can be prepared by the reduction of germanium tetrafluoride with germanium metal. It is a white solid, m.p. 110°, and is orthorhombic,  $a = 8.30$ ,  $b = 5.17$ ,  $c = 4.67$  Å. It possesses strong reducing properties.

### INTRODUCTION

Evidence for the existence of germanium difluoride was noted by Winkler (1), who heated potassium fluorogermanate in a stream of hydrogen and obtained a dark-colored mass, an aqueous extract of which yielded germanous sulphide with hydrogen sulphide. The only other description of a difluoride of germanium is that given by Dennis and Laubengayer (2) and it is their findings which are widely quoted. They characterized the fluoride as a white, sublimable, hygroscopic solid which disproportionated on heating. An aqueous solution of it possessed the reducing properties of divalent germanium but the identity of the solid was not established by analysis.

We have prepared material similar to the latter and have proved it to be germanium difluoride. Some of the physical and chemical properties of the compound have also been examined.

### DISCUSSION AND RESULTS

Dennis and Laubengayer prepared the difluoride by passing the gaseous tetrafluoride, produced by the pyrolysis of barium hexafluorogermanate, over powdered germanium, above 100°. We repeated this procedure and undoubtedly germanium difluoride was formed, but on no occasion was a sufficiently large or pure sample secured for analysis. The difluoride prepared in this way could not be transferred by distillation nor by pouring of the melt, without extensive interaction with the glass and disproportionation. These difficulties were associated with the presence of impurities, including water and hydrogen fluoride, as was manifest from the etching of the glass apparatus and may account for the delay in substantiating the earlier reports of the difluoride.

When germanium tetrafluoride was used which had been prepared by the direct fluorination of germanium metal, under strictly anhydrous conditions, the reduction proceeded smoothly and extensively in the temperature range 150–300° and in this way gram samples of the compound could be prepared and transferred without decomposition.

The stoichiometry,  $\text{GeF}_2$ , was established by germanium and fluorine analysis and the divalency was confirmed by iodine titration.

The white solid, m.p. 110°, distills without decomposition *in vacuo* at temperatures slightly above the fusion point. At higher temperatures disproportionation begins, as indicated by the appearance of an orange-red solid together with the concurrent evolution of germanium tetrafluoride. With some samples the temperature of decomposition was above 160° but since the decomposition is evidently catalyzed by impurities it is possible that more thermally stable material than this can be made. As the temperature is raised the orange-red product becomes red-brown and finally black, the last being associated

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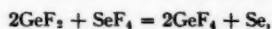
Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia.

with the presence of germanium metal. This behavior resembles that of germanium dichloride and it is probable that the orange-red intermediate is a polymeric subfluoride  $(\text{GeF})_x$ , since a similar material  $(\text{GeCl})_x$  has been reported as arising from the thermal decomposition of the dichloride (3, 4).

In ordinary moist air the difluoride deliquesces and on prolonged exposure orange germanous hydroxide separates. A mild exothermic hydrolysis occurs with water and the hydroxide precipitates. The fluoride is, however, totally soluble in 48% hydrofluoric acid and this solution has reducing properties, silver being deposited in the cold from a silver nitrate solution. The fluoride also dissolves in ethanol and forms an etherate with diethyl ether, but is insoluble in carbon tetrachloride.

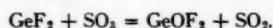
The reducing properties expected to be associated with divalent germanium have been illustrated in several reactions.

Selenium tetrafluoride is reduced to selenium by the difluoride, which is oxidized to the tetrafluoride. The germanium tetrafluoride combines with excess selenium tetrafluoride to give the crystalline solid, fluoroselenonium hexafluorogermanate. The sequence of reactions is

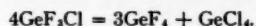
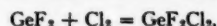


The latter material, which will be an acid in the solvent selenium tetrafluoride, is isostructural with the acids  $(\text{SeF}_4)_2\text{PtF}_4$  and  $(\text{SeF}_4)_2\text{PdF}_4$ , prepared recently in this laboratory. Details of these and other fluoroselenonium compounds will be given in a forthcoming communication.

The  $\alpha$  form of sulphur trioxide is reduced explosively by the difluoride, when the mixture is warmed, the reaction probably being



Liquid chlorine combines rapidly with the difluoride to produce a mixture containing germanium tetrafluoride, germanium tetrachloride, and chlorofluorides of germanium. The failure to prepare pure germanium dichlorodifluoride is in agreement with the observation of Booth and Morris (5) that this compound changes to a mixture of the tetrafluoride and the tetrachloride. The reaction sequence is probably



Iodine in ether solution reacts with the difluoride to give germanium tetraiodide,



It would appear that germanium difluoride will be a useful reducing agent for the preparation of lower fluorides of the transition metals and certain aspects of this work are in hand.

Germanium difluoride, like its congeners arsenic trifluoride and selenium tetrafluoride, possesses a nonbonding valence electron pair. The steric effect of the nonbonding electron pair is evident in the molecular structure of both arsenic trifluoride (6) and selenium tetrafluoride (7). A similar steric influence is evidently responsible for the absence in the difluoride of the hexagonal (low quartz) and tetragonal (rutile) arrangements found (8, 9) in the two forms of germanium dioxide. These require, respectively, regular tetrahedral and octahedral co-ordination of the germanium atom. The X-ray powder pattern

of the difluoride was indexed on the basis of an orthorhombic unit cell  $a = 8.30$ ,  $b = 5.17$ ,  $c = 4.67$  Å. As there are no systematic absences of general  $hkl$  reflections the cell must be primitive. A density measurement shows that it contains four molecules.

In view of the low melting point and the volatility of the compound it is probable that a pseudotetrahedral co-ordination of the germanium atom with three fluorine atoms and a nonbonding electron pair would be more likely than an approximate hexaco-ordination. A pseudotetrahedral arrangement would result in a selenium dioxide type of structure (10) with the pseudo tetrahedron sharing fluorine atoms to form chains. It is perhaps not without significance that the cell dimensions  $a = 8.35$ ,  $c = 5.05$  Å (10) of the tetragonal unit cell of selenium dioxide are very similar to two of the dimensions of the germanium difluoride unit cell.

## EXPERIMENTAL

### *Apparatus and Techniques*

Pyrex glass apparatus was used in the various experiments and when silica was incorporated it was joined to the glass by graded seals.

Progressive hydrolysis of the fluorides and etching of the apparatus was avoided by rigidly excluding water. All glassware was heated strongly under vacuum with a luminous flame and in those experiments conducted at atmospheric pressure, ingress of moisture was prevented by using U traps immersed in liquid oxygen.

### *The Preparation of Germanium Tetrafluoride*

The tetrafluoride was made by the fluorination of germanium metal (arsenic content 0.05 p.p.m., as supplied by Johnson, Matthey & Co. Ltd.) contained in a shallow bed in a 12-mm clear silica tube joined to a train of collecting traps, each one of which was provided with a break seal. Fluorine, diluted with nitrogen, was passed and the combustion of the germanium, which burned with a blue-green flame, was initiated with the heat from a small flame.

Apart from germanium tetrafluoride, silicon tetrafluoride was also formed, the latter arising from interaction of fluorine with the container and both products were collected at liquid oxygen temperature. By allowing the traps to warm to about  $-90^\circ$ , most of the silicon fluoride was removed in the nitrogen stream used to purge the apparatus of fluorine. Each trap was sealed under vacuum, after recooling to liquid oxygen temperature, and was kept at  $-180^\circ$  until required.

### *The Reduction of Germanium Tetrafluoride*

The most satisfactory preparation of the difluoride used lump germanium metal of the same quality as that employed above. The pieces of metal were approximately 4–5 mm in diameter and were arranged along the bottom of a 12-mm glass tube, at each end of which was joined a pair of traps. A side arm, provided with a break seal to collect the product, was situated beyond the metal and the reduction was carried out with the tetrafluoride streaming over the metal towards the side arm. In this way the product collected in the neighborhood of the side arm and was readily melted into it.

Germanium tetrafluoride, from the storage break-seal bottles, was transferred under vacuum into the appropriate set of traps, whence it was slowly passed to the second set beyond the germanium metal and the collecting side arm. With the tetrafluoride passing in this direction, reduction was affected by heating the metal with a very small flame, to maintain the temperature in the range  $150$ – $300^\circ$ . The difluoride collected on the cooler glass as a colorless liquid which rapidly crystallized. Unchanged tetrafluoride condensed



in the second set of traps, cooled in liquid nitrogen. When this transference was complete, the germanium was cooled and the tetrafluoride retransferred to the first set of traps, prior to continuation of the reduction of the gas. Since the reduction took place slowly, 10 or more passings of the tetrafluoride over the metal were usually necessary to make a 1- to 2-g sample.

Attempts to improve the speed and efficiency of the reduction were abandoned when it was found that finely powdered germanium metal transferred in the gas streams and contaminated the product, which disproportionated to or was reduced to an orange product, in the presence of the metal.

When germanium tetrafluoride was used, as prepared by the pyrolysis at 600–700°, of barium hexafluorogermanate contained in a silica bulb joined to an apparatus similar to that described above, the germanium metal became inactive after the formation of only small quantities of difluoride. These samples disproportionated at lower temperatures than the more pure material and the evidence of etching indicated that hydrogen fluoride, presumably arising from impure barium fluorogermanate, was responsible for this behavior. Drying of the barium salt at 200° *in vacuo* did not overcome these difficulties.

The difluoride melted at 110° and could be distilled *in vacuo* at 130°. Disproportionation, indicated by gas evolution and the appearance of a solid orange phase, began in some samples above 160°, the color of the product changing to orange-red to red-brown to black, as the temperature rose to 200°. The decomposition temperature was, however, markedly dependent upon the purity of the material and one sample showed only slight decomposition at 180°.

**Analysis:** A 2-g sample of the fluoride was dissolved in a mixture of ammonium hydroxide and hydrogen peroxide, the solution being subsequently boiled to destroy excess of the latter. Aliquots were taken for fluorine and germanium estimation. Fluorine was determined as lead chlorofluoride in the fluosilicic acid, hydrofluoric acid distillate produced by distilling the solution with sulphuric acid at 132–138°. The purity of the lead chlorofluoride was checked by determination of chlorine as silver chloride. Germanium was estimated as magnesium orthogermanate (11). Found: Ge, 65.6; F, 34.8%.  $\text{GeF}_2$  requires: Ge, 65.6; F, 34.4%. A second sample was dissolved in dilute sulphuric acid and was titrated against *N*/10 iodine solution. One mole required 1.92 equivalents of iodine.

**X-Ray powder photograph.**—A 0.5-mm Pyrex capillary was charged with the finely powdered difluoride, the dry-box technique being employed. Photographs were taken using a 14.32-cm camera and  $\text{Cu-K}_\alpha$  radiation in conjunction with a nickel filter. See Table I for the X-ray data.

#### *Behavior with Miscellaneous Solvents*

**Water.**—The difluoride was instantly hydrolyzed in a mild exothermic reaction. The initial yellow precipitate of germanous hydroxide rapidly turned orange. The filtrate decolorized permanganate and precipitated silver from a nitrate solution.

**48% Hydrofluoric acid.**—The fluoride was completely soluble in the acid and the solution possessed the reducing properties of the aqueous extract.

**Ethanol.**—The fluoride dissolved readily in the anhydrous solvent.

**Diethyl ether.**—The fluoride dissolved in dry ether but a white solid crystallized slowly from this solution. Evaporation of the ether *in vacuo* led to the breakdown of this solid, leaving what appeared to be germanium difluoride. The etherate was not investigated further.

**Carbon tetrachloride.**—A small particle of the difluoride remained undissolved by approximately 20 cc of the tetrachloride.



TABLE I  
Calculated and observed X-ray data for  $\text{GeF}_2$

hkl	1/d <sup>2</sup>		Relative intensities, I	hkl	1/d <sup>2</sup>		Relative intensities, I	hkl	1/d <sup>2</sup>		Relative intensities, I
	Calc.	Obs.			Calc.	Obs.			Calc.	Obs.	
101	.0519	.0524	w	205	.5123	.5136	vw	502	.9943	.9922	vw
011	.0602	.0604	m	313	.5132			243	1.0115	1.0117	mw
110	.0832	.0832	vs	006	.5220	.5232	vw	118	1.0112		
102	.0955	.0956	s	025	.5453	.5457	w	512	1.0400	1.0402	w
111	.0977	.0975	m	230	.5611	.5618	w	326	1.0422		
012	.1037	.1035	s	106	.5594			503	1.0668	1.0663	w
112	.1412	.1418	w	224	.5646	.5659	w	341	1.0827	1.0815	w
200	.1498	.1499	m	322	.5778	.5785	mw	236	1.0838		
103	.1680	.1692	vw	400	.5992	.5995	vw	335	1.1108		
013	.1762	.1765	vw	314	.6147	.6157	mw	028	1.1108	1.1111	vw
020	.1828	.1834	w	232	.6191	.6183	mw	513	1.1125		
210	.1955	.1966	vw	034	.6433	.6442	vw	342	1.1262	1.1255	vw
202	.2078	.2076	vw	134	.6808	.6812	vw	416	1.1669	1.1648	vw
004	.2320	.2333	w	007	.7105	.7093	w	009	1.1745	1.1769	vw
212	.2535	.2543	s	216	.7175	.7177	w	218	1.1775		
104	.2694	.2714	vw	040	.7312	.7304	vw	514	1.2140	1.2132	vw
122	.2782	.2787	ms	403	.7297			228	1.2606	1.2603	vw
114	.3151	.3162	ms	126	.7422	.7420	vw	146	1.2906	1.2890	vw
213	.3260	.3245	vw	041	.7457	.7460	vw	250	1.2912		
220	.3326	.3337	m	315	.7452			407	1.3097	1.3092	vw
300	.3370	.3398	vw	331	.7628	.7653	vw	530	1.3476	1.3466	vw
123	.3508	.3519	vw	420	.7820	.7827	w	515	1.3445		
310	.3827	.3834	ms	404	.8312	.8297	w	435	1.3749	1.3730	vw
302	.3950	.3955	m	043	.8617	.8589	vw	0010	1.4500	1.4498	vw
024	.4148	.4160	ms	306	.8590			328	1.4482		
031	.4267	.4272	vw	240	.8810	.8805	vw	620	1.5310	1.5296	vw
130	.4496	.4498	w	217	.9308	.9306	vw	444	1.5624	1.5630	vw
223	.4631	.4634	vw	044	.9632	.9633	vw	604	1.5802	1.5776	vw
032	.4693	.4718	w	334	.9803	.9807	w				

vs > s > ms > m > mw > w > vw > vv

#### The Determination of the Density of the Solid

A 2-ml-capacity density bottle, provided with a ground-glass cap, was loaded in a dry box. All weighings were made with the bottle and its contents at 23°. Carbon tetrachloride was employed as the displacement fluid.  $d_{23}^\circ = 3.7$  g/cc.

With four molecules per unit cell ( $a = 5.17$ ,  $b = 4.67$ ,  $c = 8.30$  Å),  $d_{\text{calc}} = 3.66$  g/cc.

#### The Reaction of Germanium Difluoride with Selenium Tetrafluoride

Selenium tetrafluoride prepared as described by Aynsley, Peacock, and Robinson (12) was transferred by vacuum distillation to a bulb at  $-180^\circ$ , situated beneath an upturned break-seal bottle containing a sample of the difluoride. This sample was melted down on to the excess of selenium tetrafluoride. The difluoride dissolved in the selenium fluoride when the mixture was warmed to  $20^\circ$ . Green colloidal selenium was produced almost immediately and this rapidly transformed to red selenium. As the reaction proceeded a white solid also crystallized from the solution. When the reaction was judged to be complete the excess of selenium tetrafluoride was removed by vacuum distillation and a residue of red selenium and a white solid remained. The latter sublimed at ca.  $100^\circ$  (1 atm).

An X-ray powder photograph of the residual mixture was taken, in the manner described.

### *The Preparation of $(\text{SeF}_4)_2\text{GeF}_4$*

An excess of germanium tetrafluoride was mixed with selenium tetrafluoride at atmospheric pressure. A white solid formed immediately. The excess of germanium tetrafluoride was removed under vacuum at  $0^\circ$ . This solid sublimed at ca.  $100^\circ$  (1 atm). An X-ray powder photograph of the solid was taken and the pattern was found to conform with the major pattern of the residue from the selenium tetrafluoride-germanium difluoride reaction.

Analysis: A weighed sample was dissolved in sodium carbonate solution and aliquots were analyzed for selenium, which was determined as the element by reduction with sulphurous acid in strong hydrochloric acid solution, and fluorine which was determined as previously described. Found: Se, 34.4; F, 51.0%.  $(\text{SeF}_4)_2\text{GeF}_4$  requires: Se, 34.5; F, 49.7%.

### *Germanium Difluoride with $\alpha$ -Sulphur Trioxide*

Liquid sulphur trioxide was prepared by the distillation of 60% oleum with phosphorus pentoxide, followed by a second distillation from phosphorus pentoxide. The apparatus used for this preparation was rigorously dried and ingress of moisture was prevented by three U traps, in series, at  $-180^\circ$ . A sample of the trioxide was distilled under vacuum into a break-seal bottle cooled in ice.

A break-seal bottle (cooled in ice) containing a sample of germanium difluoride was opened and sulphur trioxide was distilled into it, under vacuum. The apparatus was opened to the air via a series of U traps immersed in liquid oxygen and the mixture was allowed to warm to room temperature. The difluoride did not dissolve noticeably in the liquid trioxide up to  $25^\circ$  and when the mixture was warmed there was an explosion which destroyed the containing bottle.

### *Germanium Difluoride with Chlorine*

Chlorine was melted on to a 0.5-g sample of the difluoride. The immediate and vigorous reaction, which followed, was moderated by cooling with liquid oxygen. On completion of the reaction, excess chlorine was removed from the mixture under vacuum at  $-78^\circ$  and a colorless liquid remained. A gas, which condensed to a white solid was removed with the chlorine. This solid resembled germanium tetrafluoride.

The colorless liquid which had a vapor pressure of 20 cm at  $24^\circ$  transferred rapidly and completely in a vacuum, at room temperature. Anal. Found: mol. wt., 197. Calc.: mol. wt.  $\text{GeF}_2\text{Cl}_2$ , 181.6; mol. wt.  $\text{GeFCl}_3$ , 198.1;  $\text{GeCl}_4$ , 214.6.

Infrared spectra of successive fractions of the vapor showed a strong absorption band at  $740\text{ cm}^{-1}$ , indicative of Ge—F stretching. There was no band at  $800\text{ cm}^{-1}$ , which is the location for a strong germanium tetrafluoride absorption band (13). A small peak at  $1050\text{ cm}^{-1}$  showed silicon tetrafluoride (arising from fluoride attack on the glass apparatus) to be present in low concentration.

A gravimetric analysis for chlorine as silver chloride was made on the least volatile fraction of the liquid. Found: Cl, 60.8%. Calc. for  $\text{GeCl}_4$ : Cl, 66.4%; for  $\text{GeFCl}_3$ : Cl, 53.7%. Although both  $\text{GeF}_2\text{Cl}_2$ , b.p.  $-2.8^\circ$  (5), and  $\text{GeFCl}_3$ , b.p.  $37.5^\circ$  (5), are probably present, it is not possible at this time to say which of the chlorofluorides predominates in the mixture with germanium tetrachloride.

### *Germanium Difluoride with Iodine*

A solution of iodine in ether was added to a suspension of germanium difluoride in ether, until the iodine color persisted. Evaporation of the ether under vacuum left an

orange residue. This was washed with a small quantity of ether and was dried in a vacuum. It was identified as germanium tetraiodide, m.p.  $146^{\circ}$ , literature value  $146^{\circ}$ . (14).

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# THE DECOMPOSITION OF METHANE IN THE NEGATIVE GLOW<sup>1</sup>

A. W. TICKNER

## ABSTRACT

The decomposition of methane was studied in the negative glow of a d-c. discharge at pressures of 0.30 and 0.050 mm. The discharge tube was cooled by liquid or solid nitrogen.

The main products were ethane, ethylene, and acetylene in addition to hydrogen and a nonvolatile product which appeared mainly on the cathode as a solid having the formula  $(CH)_n$ . Smaller amounts of propane, propene, propyne, butane, butene, butadiene, and pentene were also found. Lowering the temperature of the discharge tube from  $-196^\circ$  to  $-210^\circ$  C greatly increased the amount of ethylene recovered.

The solid product is apparently transported to the cathode in the form of ions and may result from ionic polymerization of the acetylene. Acetylene is the volatile product formed closest to the cathode which suggests that it may also be formed by ionic processes. The formation of the remaining products is consistent with an excitation mechanism in which the  $C_2$  products are formed first and the higher hydrocarbons are formed from them.

## INTRODUCTION

The decomposition of methane in the glow discharge has been studied for many years; the early work is summarized in reference 1. More recently, Yeddanapalli (2) studied the decomposition of methane in a d-c. glow discharge using a discharge tube cooled in liquid air. He worked at pressures of a few millimeters and found that the products consisted of ethane, ethylene, and acetylene as well as hydrogen and a nonvolatile product having the formula  $(CH_2)_n$ . Wiener and Burton (3), using a d-c. glow discharge at atmospheric pressure, showed that under conditions of high conversion and relatively high temperature the only significant products were acetylene, hydrogen, and carbon. McCarthy (4) found that, in addition to acetylene, ethylene and ethane were obtained as products when the gas from a microwave discharge in methane was allowed to impinge directly on a wall cooled by liquid nitrogen.

The low-pressure d-c. glow discharge is suitable for investigations of this type because it permits studying the decomposition in a number of different discharge regions for which the electrical processes are reasonably well understood (5, 6). In addition, the vapor pressures of methane and its decomposition products are such that most of the products can be removed rapidly from the reaction by freezing them out on the discharge tube wall. There is thus the possibility of obtaining direct information about the primary products of the decomposition. This approach was used by Yeddanapalli (2), whose work, however, had two main weaknesses: (a) at the temperature of liquid air the vapor pressure of ethylene is sufficiently high that much of it would have remained in the gas phase, and (b) his method of analysis was such that the products were determined as acetylene and ethylene with the remainder assumed to be ethane. Any higher hydrocarbons which might have been formed would thus not have been detected.

The negative glow was chosen as a suitable region with which to begin a study of the decomposition of methane in the electric discharge. It was known to be a region of great chemical activity which could be to a considerable degree operated independently of other discharge regions. The experiments reported here were intended primarily to clarify the work of Yeddanapalli and to serve as a basis for a more detailed study of the discharge decomposition. In order to recover the first products more completely, temperatures lower than those in the earlier work have been used. The use of a direct pumping system

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instead of the circulating system previously employed (2) enabled the experiments to be carried out at constant pressure and reduced the residence time in the discharge zone.

#### EXPERIMENTAL

The experiments were carried out in the apparatus shown diagrammatically in Fig. 1. It consisted of a jacketed discharge tube with a fixed cathode and an anode which could be moved by a rack and gear as shown. The discharge tube diameter of 3.4 cm was

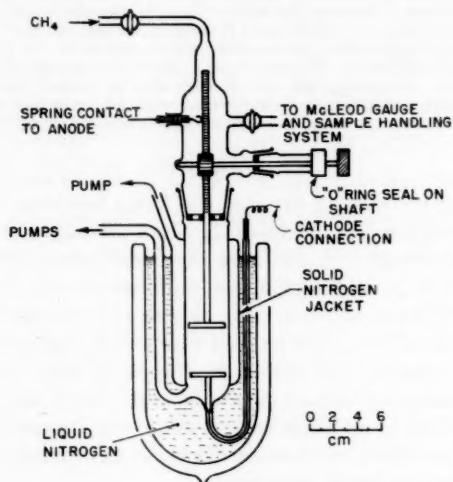


FIG. 1. Discharge tube.

chosen as a reasonable compromise between the requirements for efficient trapping of products (small diameter) and ideal glow discharge conditions (large diameter). The electrodes were 3.0 cm in diameter and were made of stainless steel. A mercury diffusion pump with a pumping speed of 10 liters per second and a forepump allowed the system to be evacuated to pressures of less than  $10^{-6}$  mm of mercury. The residence time in the discharge zone with the electrodes placed to include the entire negative glow was 0.05 second for a discharge pressure of 0.3 mm and 0.5 second for a discharge pressure of 0.05 mm. Pressures were measured by a small McLeod gauge.

A variable voltage d-c. power supply having a ripple of less than 0.1 volt supplied power to the discharge through a 10,000-ohm series resistor. The discharge current was controlled manually.

The discharge tube was cooled by filling the jacket with liquid nitrogen and pumping on it until the nitrogen solidified. By controlling the pumping speed it was possible to maintain a constant pressure over the nitrogen in the jacket and thus to maintain a constant discharge tube wall temperature for a period of about 15 minutes. Temperatures down to  $-220^{\circ}\text{C}$  could be obtained in this way. The temperature of the discharge tube wall was determined by measuring the vapor pressure of methane corresponding to a given jacket pressure and comparing this with the vapor pressure of methane as given by Ziegler (7).

The methane used was Matheson C.P. grade; it was purified by fractional distillation



before admitting it to the storage reservoir. Its flow rate was controlled by a needle valve and it was admitted through a trap maintained at either the temperature of liquid nitrogen or the triple point of nitrogen depending upon the methane pressure being used. When necessary a correction was made for the small amount of ethane which was found to be present in blank runs.

The lengths of the negative glow and cathode dark space were determined by measuring the voltage drop across the discharge for various electrode spacings at constant discharge current (5). For the purpose of this work the length of the cathode dark space was taken as equal to the electrode spacing at which the voltage began to rise steeply when the anode was being moved towards the cathode. The anode end of the negative glow was taken as equal to the electrode spacing at which the voltage began to increase when the anode was being moved away from the cathode.

The experiments were performed by cooling the discharge tube to the required temperature, establishing the methane flow, and operating the discharge for a suitable period which in practice varied from 3 to 12 minutes. After the discharge was turned off, the discharge tube was pumped briefly to a low pressure, isolated, and warmed to room temperature. The volatile products were then transferred to a gas burette for measurement and analyzed on a mass spectrometer. The carbon content of the non-volatile discharge product was determined by oxidizing it *in situ* with an oxygen discharge and measuring the carbon dioxide produced. The method has been described previously (8).

## RESULTS

Preliminary experiments demonstrated that the amount of ethylene recovered at about 1% methane decomposition increased nearly 10-fold when the discharge tube temperature was lowered from that of liquid nitrogen ( $-196^{\circ}\text{C}$ ) to the triple point of nitrogen ( $-210^{\circ}\text{C}$ ). The amount of ethane recovered also increased by about one-third and some of the higher products, especially propene and butene, decreased in amount. Extrapolation of the existing vapor pressure data for ethylene and ethane (7) indicates that their vapor pressures are less than  $10^{-6}$  mm at  $-210^{\circ}\text{C}$ . Thus, the recovery of these products should be practically quantitative at this temperature, assuming equilibrium at the wall.

In several experiments at approximately 2% methane decomposition the gas downstream from the discharge was sampled and analyzed on a mass spectrometer. In each case the amount of hydrogen found agreed, within the accuracy of the analysis, with that calculated on the basis of the products formed.

The variation of the products with discharge current was studied in a series of experiments at a pressure of 0.30 mm, which is the vapor pressure of methane at  $-210^{\circ}\text{C}$ . The electrode spacing used was 3.0 cm, equal to the length of the negative glow at this pressure. The results are shown in Fig. 2. The amount of methane decomposed was calculated from the composition of the products; the percentage decomposition was 0.5% for a current of 1 ma. Values shown for the nonvolatile product give its carbon content in gram-atoms. In these experiments the voltage drop across the discharge increased from 330 volts for a current of 1 ma to 390 volts for a current of 4.5 ma.

A pressure of 0.05 mm was chosen as a convenient one for most of the experiments. The choice of a lower pressure made control of the wall temperature less critical and reduced the number of collisions undergone by product molecules in diffusing to the cold wall. In addition, the increased lengths of the cathode dark space and the negative



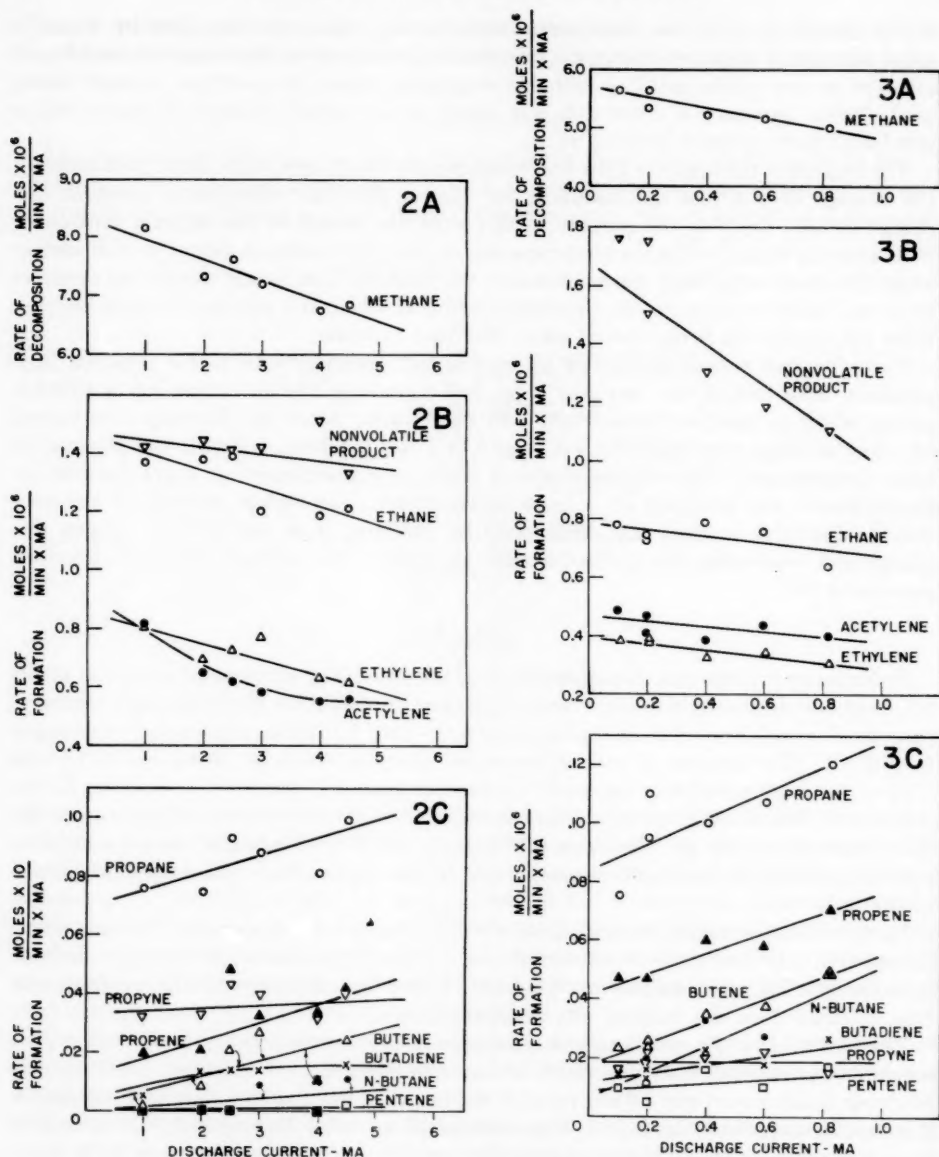


FIG. 2. Effect of discharge current on the decomposition of methane in the negative glow at  $-210^{\circ}\text{C}$ . Methane pressure, 0.30 mm. Electrode spacing, 3.0 cm.

FIG. 3. Effect of discharge current on the decomposition of methane in the negative glow at 0.050-mm pressure. Electrode spacing, 10 cm. Temperature,  $-213^{\circ}\text{C}$ .

glow made it easier to detect any variation in the products along the discharge. A wall temperature of about  $-213^{\circ}\text{C}$  was used in experiments at this pressure.

The effect of discharge current on the rates of formation of the products at a pressure of 0.050 mm is shown in Fig. 3. An electrode spacing of 10 cm was used, corresponding to the length of the negative glow at this pressure. A discharge current of 0.10 ma corresponded to 0.6% decomposition of the methane. The discharge voltage increased from 385 volts for a current of 0.10 ma to 750 volts for a current of 0.82 ma.

Hydrogen was the only product whose effect on the reaction could be conveniently tested. Figure 4 gives the results of a series of experiments in which hydrogen was added to the methane to give mixtures having total hydrogen contents of up to 20 mole%. The hydrogen formed in the decomposition was taken into account in calculating the compositions of the mixtures.

The distribution of products along the negative glow was studied in another series of experiments in which the electrode spacing was varied. The results are shown in Fig. 5. As the anode was moved towards the cathode the negative glow was eliminated progressively from the anode end. This appeared to have little effect on the operation of the discharge until the edge of the cathode dark space was reached at an electrode spacing of about 1.8 cm. In order to make the experiments comparable over as wide a range as possible a discharge current of 0.50 ma was chosen; lower currents could not be maintained at the smallest electrode spacings used.

The nonvolatile product which formed in the discharge experiments was visible only as a solid deposit on the cathode. This deposit appeared to be a continuous film and interference colors showed it to be of uniform thickness over the area of the electrode covered. In one of the experiments at a pressure of 0.05 mm a flat Pyrex disk having a diameter of 4 mm and a thickness of 0.025 mm was placed on the surface of the cathode. Although a uniform and readily visible deposit was formed on the cathode all around the disk, and extending up to the edge of it, no deposit was visible on the disk itself. It appeared therefore that the deposit was formed only on that part of the cathode which was bombarded by incoming ions.

In order to obtain enough of the cathode deposit for a chemical analysis, several experiments were carried out in which the discharge was operated for periods of about 30 minutes at currents of 7 or 8 ma. The upper electrode was made the cathode in these experiments to facilitate the removal of the deposit. Two samples of about 2 mg each, obtained at the temperature of liquid nitrogen, gave analyses corresponding to  $C_{1.00}H_{1.01}$  and  $C_{1.00}H_{1.02}$ . In another experiment the liquid nitrogen level was maintained about 1 cm below the cathode in order to reduce the possibility that a deposit of frozen product gases was contributing to the formation of the solid. Analysis of this sample gave a composition represented by  $C_{1.00}H_{0.75}$ . A further sample of the cathode deposit, prepared by operating the discharge at room temperature, was found to have the composition given by  $C_{1.00}H_{0.70}$ . Although the removal of the solid from the cathode was not quantitative the amount recovered accounted in every case for more than half the nonvolatile product calculated to be formed on the basis of the results in Fig. 2. It seems probable therefore that the cathode deposit accounts for nearly all of the nonvolatile product. The only evidence of any other accumulation of a nonvolatile product was the appearance of interference colors on the anode during these experiments. This may have indicated the formation there of much smaller quantities of another solid product.

It was not possible to determine from the mass spectra whether the product which appeared at  $m/e = 42$  was propene or cyclopropane. This product was separated from the others by gas chromatography and shown to be propene.

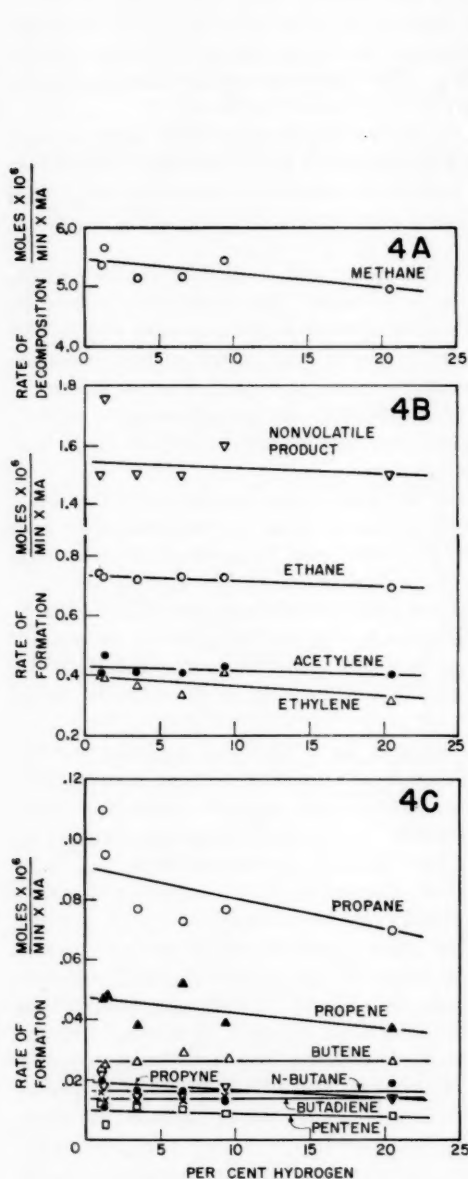
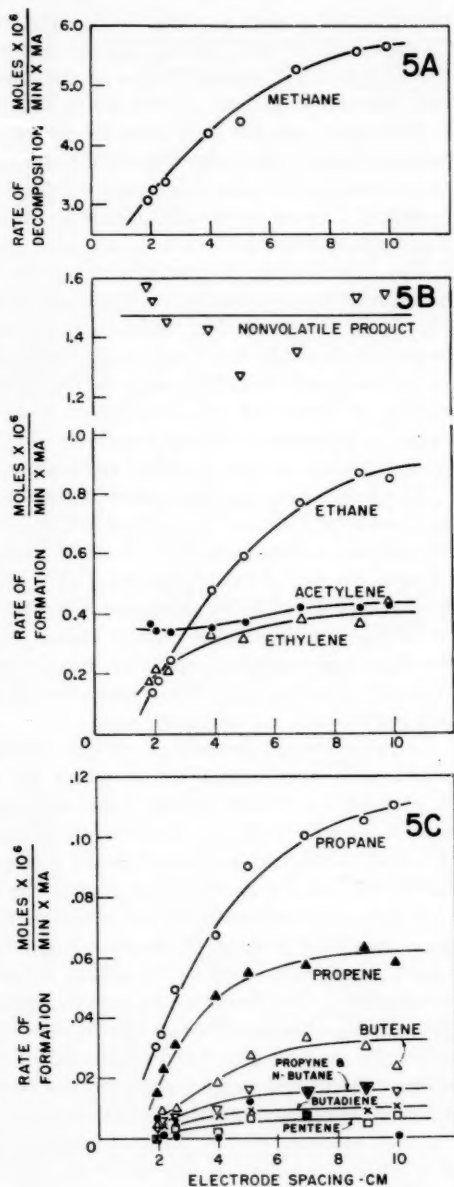


FIG. 4. Effect of hydrogen on the decomposition of methane in the negative glow. Total pressure, 0.050 mm. Current, 0.20 ma. Electrode spacing, 10 cm. Temperature,  $-213^{\circ}\text{C}$ .

FIG. 5. Effect of electrode spacing on the decomposition of methane. Pressure, 0.050 mm. Current, 0.50 ma. Temperature,  $-213^{\circ}\text{C}$ .



## DISCUSSION

The products obtained in this work were considerably more complex than those obtained by Yeddanapalli (2). This was due mainly to the improved analytical technique used. In addition, the increased recovery of ethylene at wall temperatures of  $-210^{\circ}\text{C}$  or lower indicates that the yield of ethylene found by Yeddanapalli was too low because much of it would not have been removed from the reaction at the temperature of liquid air. Instead of a polymer having the formula  $(\text{CH}_2)_n$  as indicated by Yeddanapalli's results, the nonvolatile product was found to consist mostly of a solid of formula  $(\text{CH})_n$  which appeared on the cathode.

Yeddanapalli's conclusion that the rate of decomposition in the negative glow is proportional to the current and independent of the pressure holds only approximately for these experiments which extend into the abnormal discharge region. The electron efficiency in this work is defined as the number of methane molecules decomposed per electron charge carried by the current. In the experiments at 0.30-mm pressure (Fig. 2), for which the discharge is nearly normal, the electron efficiency decreases from 12.8 at 1.0 ma to 10.7 at 4.5 ma. At 0.050 mm where the discharge is more abnormal the electron efficiency decreases from 9.0 at 0.10 ma to 8.0 at 0.82 ma. These values are to be compared with the average value of 10 obtained by Yeddanapalli (2) at pressures ranging from 2 to 9 mm and discharge currents between 10 and 30 ma. It is evident that the electron efficiency for the negative glow plus the cathode dark space is approximately 10 over a fairly wide range of discharge conditions.

The products found in these experiments are very similar to those found by Manton and Tickner (9) in their study of the decomposition of methane by a beam of electrons. Since it is known that the electrons in the negative regions of a d-c. glow discharge possess beam properties and have energies similar to those used in the electron beam experiments, this suggests that the products of the negative glow are formed by a mechanism similar to the one which they proposed. The higher electron efficiencies obtained in the glow are accounted for by the many secondary electrons which acquire energy in the electric field, lose it in exciting gas molecules, and subsequently recombine with ions without contributing to the discharge current.

The work of Manton and Tickner indicated that the products were due mainly to excitation rather than to ionization and provided some evidence that the higher products were formed by the reaction of some species, such as excited methylene radicals, with the lower hydrocarbon products. The results obtained here are consistent with this mechanism. In the experiments at both 0.30 mm (Fig. 2) and 0.050 mm (Fig. 3) the yields of the  $\text{C}_2$  products fall off with increasing current while the yields of the higher hydrocarbons increase. Also, lowering the discharge tube temperature from  $-196^{\circ}\text{C}$  to  $-210^{\circ}\text{C}$  while greatly increasing the recovery of ethylene resulted in a decrease in the amounts of propene and butene. Thus, there seems to be definite evidence that the higher hydrocarbons are formed at the expense of the  $\text{C}_2$  products.

It has been suggested (10) that the addition of excited methylene to a double bond often results in the formation of an energy-rich cyclic compound which may then rearrange to an olefin. Since no cyclopropane is found among the discharge products there is no evidence of this kind that excited methylene is the active species.

The addition of hydrogen to the methane in concentrations up to 20 mole% appears to have little effect on the products. The small lowering of all yields as the concentration of hydrogen is increased is consistent with the explanation put forward by Yeddanapalli that hydrogen behaves as a diluent, absorbing some of the electrical energy. Since some

decomposition of the hydrogen into atoms would be expected, it seems probable that under our conditions of fast trapping the reactions of hydrogen atoms do not play an important part. It is possible, however, that the number of hydrogen atoms generated from the added hydrogen is small compared with the number formed in the methane decomposition and that for this reason the effect of the added hydrogen is not appreciable.

The results obtained by varying the distance between the electrodes (Fig. 5) indicate that the products are not formed uniformly throughout the negative glow. While it is possible that moving the anode into the glow may alter the mechanism it seems to be accepted (5) that the operation of a discharge is disturbed to a relatively small extent until the anode reaches the cathode edge of the glow. Judging by the observed current-voltage relationship this seems to hold true for these experiments. Thus, there appears to be good evidence that most of the acetylene, and possibly part of the ethylene, are formed either at the edge of the negative glow nearest the cathode or, perhaps, in the cathode dark space. The other products appear to be formed in the body of the glow although the results in Fig. 5 may indicate that the distribution is not the same for all of them.

It seems likely that the variation in the relative amounts of the various products along the glow is related to the variation in the electron energy distribution. At the cathode edge of the glow a relatively large number of electrons have sufficient energy to ionize but their number falls off rapidly with increasing distance from the cathode. In the interior of the glow, electrons of much lower energy predominate (5, 6). The fact that most of the acetylene is apparently formed in a region in which there are relatively large numbers of high-energy electrons appears to indicate that it depends on ionization for its formation. This would not be inconsistent with the findings of Manton and Tickner (9) because acetylene constituted a relatively small part of the total product on which their conclusions were based. The remaining products are formed in the interior of the glow where excitation processes are more important. Thus, with the possible exception of acetylene, the mechanism put forward by Manton and Tickner seems to offer a reasonable explanation of the products of the negative glow.

The conclusion that acetylene was the product formed nearest the cathode takes on interesting implications when related to the formation of the solid product. At the low temperatures and low currents used in these experiments a solid product having exactly the formula  $(CH)_n$  formed in visible quantities only on the cathode. Since no deposit formed on an insulator covering part of the cathode surface it seems likely that the solid layer was formed by the incoming ions. This conclusion is consistent with the observation that the rate of formation of the nonvolatile product was affected little by changes in wall temperature, pressure, or electrode spacing as shown in Figs. 2 to 5. Experiments in which the cathode was kept above the liquid nitrogen level or in which the discharge was operated at room temperature indicate that the deposit did not originate in a layer of acetylene frozen out on the cathode surface. Instead, these experiments provide some evidence that at higher temperatures the cathode deposit loses hydrogen under ion bombardment. These considerations lead to the conclusion that the solid product on the cathode is an acetylene polymer similar to the cuprene formed in the high-energy irradiation of acetylene (11, 12). There is a considerable amount of evidence that the cuprene formed in these irradiation studies depends on ionization for its formation (12, 13, 14). It seems possible therefore that in the glow discharge acetylene formed near the cathode becomes ionized, either directly or by charge exchange, and then polymerizes in a series of ion-molecule reactions while on its way to the cathode.



The appearance of traces of an involatile product on the anode may indicate that small amounts of a polymer are also formed by another mechanism.

#### ACKNOWLEDGMENTS

The author wishes to express his appreciation to Mr. R. L. Sander, who performed the mass spectrometric analyses, and to Mr. J. R. H. Seguin, who analyzed the solid product appearing on the cathode.

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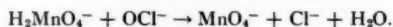
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## OXIDATION OF MANGANATE BY HYPOCHLORITE<sup>1</sup>

M. W. LISTER AND Y. YOSHINO<sup>2</sup>

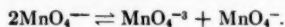
### ABSTRACT

The oxidation of potassium manganate to potassium permanganate by potassium hypochlorite has been examined. The rate of the reaction is proportional to the square of the manganate concentration and the first power of the hypochlorite, and it is inversely proportional to the permanganate concentration and to the square of the hydroxide ion concentration. It seems probable that the reaction involves the intermediate formation of hypomanganate ions from a relatively fast disproportionation of manganate, followed by a slower oxidation by hypochlorite. The following mechanism is tentatively proposed:



Data on the over-all rate and effective activation energy (19.6 kcal/g-molecule) are given; but at present it is not possible to separate all the rate constants and equilibrium constants.

The present writers have examined in a recent paper (1) the mechanism of the oxidation of manganate by periodate ions. It was found that this reaction goes chiefly through the intermediate formation of hypomanganate ions, arising from the equilibrium



The hypomanganate ions are then oxidized in a bimolecular reaction with periodate. The reaction of manganate with hypochlorite ions is at first sight a similar reaction. This reaction also takes place in alkaline solution, the over-all change being



As with periodate, the hypochlorite ion changes by two oxidation steps, while the manganate ion changes by one; so a reaction in at least two steps, or else a termolecular reaction, seemed probable. With periodate ions a termolecular reaction is largely avoided by the two-stage reaction involving hypomanganate ions. The evidence which will be given below shows that a very similar mechanism operates with hypochlorite ions.

### EXPERIMENTAL METHOD

Mixtures of potassium manganate, potassium hypochlorite, and potassium hydroxide of various concentrations were made up in aqueous solution. They were kept in a thermostat controlled to 0.1° C, and samples were taken at intervals for analysis. The reaction was followed by measuring the optical density of the solutions, mostly at 610 mμ, on a Beckmann DU spectrophotometer. This wave length is at the absorption maximum for manganate ions; the extinction coefficients used were the same as in the earlier paper (1). It was assumed that all the manganese was present either as manganate or permanganate ions. This was confirmed in several ways. Firstly the solutions showed no signs of precipitated manganese dioxide, which is the most probable alternative form for the manganese. Secondly, the total oxidizing normality of the solution (measured by adding potassium iodide and sulphuric acid, and titrating with sodium thiosulphate) was found not to change during a run. Thirdly, measurements were also made at 550 mμ, where the

<sup>1</sup>Manuscript received August 25, 1960.

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permanganate ion has an absorption maximum; the concentrations of manganate and of permanganate, calculated from the measurements at the two wave lengths, were in good agreement.

Potassium manganate was made as described by Carrington and Symonds (2). Potassium hypochlorite was made by the usual method of passing chlorine into cold potassium hydroxide solution; hence the reaction mixtures always contained potassium chloride.

The initial concentrations in various runs are given in Table I. In most of these runs

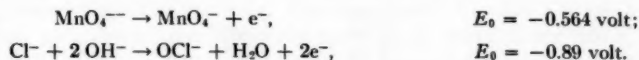
TABLE I  
Initial concentrations

Run	Temp., °C	[K <sub>2</sub> MnO <sub>4</sub> ], ×10 <sup>-4</sup> M	[KOCl], ×10 <sup>-4</sup> M	[KOH], M	[KMnO <sub>4</sub> ], ×10 <sup>-4</sup> M	Slope, ×10 <sup>2</sup>
1	35.0	3.08	100	0.094	0	6.8
2	"	4.16	100	0.106	0	6.9
3	"	2.16	100	0.099	0	7.5
4	"	3.13	100	0.049	0	29.8
5	"	3.09	10	0.049	0	3.7
6	"	3.11	20	0.103	0	1.47
7	45.0	3.08	100	0.096	0	22.0
8	25.0	3.14	100	0.106	0	2.25
9	35.0	3.15	200	0.106	0	11.9
10	"	3.19	10	0.102	0	0.70
11	"	3.19	50	0.102	0	3.5
12	"	3.15	100	0.204	0	1.97
13	"	3.15	100	0.029	0	58
14	"	2.75	100	0.098	0	5.4
15	"	3.21	100	0.100	3.00	9.1
16	"	3.03	100	0.098	1.03	7.7
17	"	3.14	100	0.0995	2.06	8.35
18	"	3.35	100	0.0995	4.12	8.9
19	"	3.21	100	0.099	3.00	9.5
20	"	3.04	100	0.030	0	63

the potassium hypochlorite was in sufficient excess so that it remained effectively constant throughout the run. The ionic strength was regulated at an initial value of 0.2 by addition of potassium nitrate. The ionic strength changed by an insignificant amount during any run.

## RESULTS

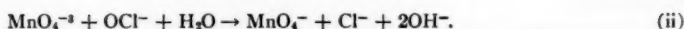
The concentrations of manganate ions at various times were calculated for all runs. These concentrations will be presented in terms of the equation that they were found to fit, as described below. At first the usual equations for a monomolecular or a bimolecular mechanism were tried, but the results did not fit these simple equations. The rate of reaction was rapid at first, but slowed up very markedly with time; in fact in some runs the rate was not far from being proportional to the fourth power of the manganate concentration. This slowing up cannot be attributed to reversibility of the reaction, as the relevant standard electrode potentials (3) are



Hence at equilibrium, for the conditions used, virtually all the manganese would be present as permanganate ions.

It was found, however, that the following mechanism gave an equation which fitted

the experimental results:



The initial equilibrium in reaction (i) is assumed to be fast relative to reaction (ii), which determines the rate. If  $k_2$  is the rate constant of the second reaction, then

$$\frac{d[\text{MnO}_4^{2-}]}{dt} = -2k_2[\text{MnO}_4^{2-}] \cdot [\text{OCl}^-]$$

as two manganate ions react to give one hypomanganate ion. If  $K$  is the equilibrium constant of reaction (i), and if the concentration of hypomanganate ion at any time is very small, then

$$[\text{MnO}_4^{2-}] = \frac{K \cdot [\text{MnO}_4^{2-}]^2}{[\text{MnO}_4^{2-}]_0 - [\text{MnO}_4^{2-}] + [\text{MnO}_4^{2-}]_0}$$

where the subscript "0" indicates the initial concentration. If we substitute this in the rate equation, and allow for the fact that the potassium hypochlorite is also used up, integration of the rate equation gives

$$(\text{A}) \quad 2K \cdot k_2 [\text{OCl}^-]_0 (1 - b/2)t = (1+w)(a-1) - [(1+wb/2)/(1-b/2)] \ln [a(1-b/2+b/2a)]$$

where

$$a = [\text{MnO}_4^{2-}]_0 / [\text{MnO}_4^{2-}],$$

$$b = [\text{MnO}_4^{2-}]_0 / [\text{OCl}^-]_0,$$

and

$$w = [\text{MnO}_4^{2-}]_0 / [\text{MnO}_4^{2-}]_0.$$

In most runs the initial hypochlorite concentration was so large that  $b$  can be taken to be negligibly small; equation (A) then reduces to

$$(\text{B}) \quad 2K \cdot k_2 [\text{OCl}^-]_0 t = (1+w)(a-1) - \ln a.$$

Equation (B) is accurate to within 1% for all runs except 5, 6, and 10, which were done with low hypochlorite ion concentrations, and even here the error in the calculated rate constants by using equation (B) would be about 5%. Equation (A) was used for these runs.

If this theory of the reaction mechanism is correct, then a plot of  $[(1+w)(a-1) - \ln a]$  against time should be linear. These plots are shown in the figures, and do in fact give straight lines for all runs. Data for a typical run are:

Run 1;  $w = 0$

Time, minutes	$[\text{MnO}_4^{2-}]$ , $\times 10^{-4} M$	$[a-1-\ln a]$	Time, minutes	$[\text{MnO}_4^{2-}]$ , $\times 10^{-4} M$	$[a-1-\ln a]$
0	3.08	0	26	1.84	0.159
1	2.92	0.002	34	1.72	0.208
2½	2.74	0.007	43	1.61	0.264
4	2.62	0.014	57	1.45	0.371
6	2.45	0.028	70	1.34	0.466
9	2.32	0.044	90	1.22	0.598
13	2.19	0.066	110	1.12	0.738
18	2.03	0.105	131	1.04	0.876

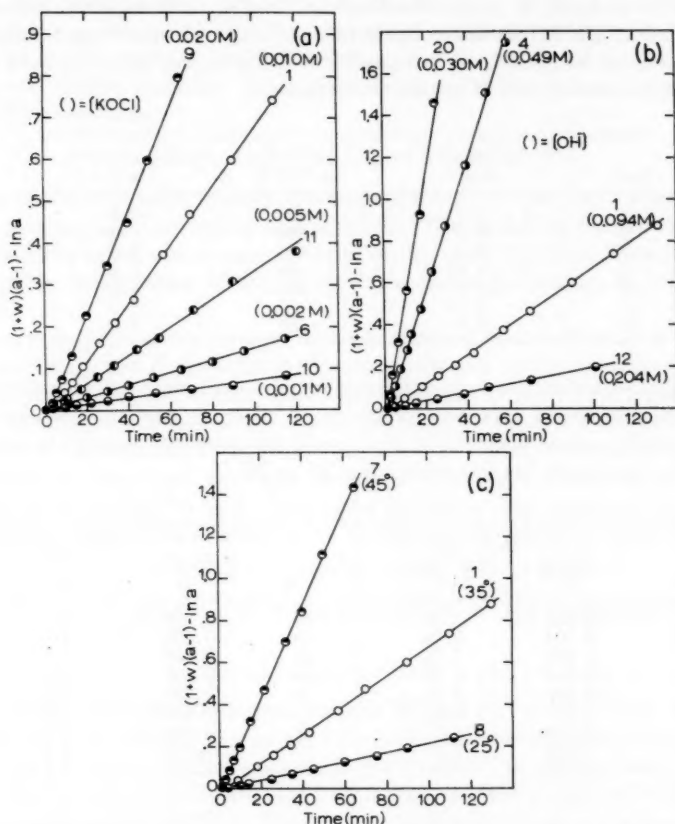


FIG. 1. Results showing agreement of experiment with equation (B). (a) Effect of hypochlorite concentration. (b) Effect of hydroxide concentration. (c) Effect of temperature.

In many runs there is a slight deviation from a straight line initially. This is partly due to the assumption that initially  $[\text{MnO}_4^-]$  is zero, while in practice reaction (i) would inevitably provide a small quantity of permanganate. Once the reaction has started, errors due to this approximation will rapidly become negligible. However, this effect is in general not large enough to account for the observed deviation, which is presumably due to a trace of permanganate present as an impurity in the potassium manganate. Apart from the points obtained during the first few minutes of any run, the experimental points, plotted according to equation (B), always fell on a straight line.

A further argument in favor of the above mechanism is that addition of potassium permanganate does in fact slow down the reaction. This was found in runs 15, 16, 17, 18, and 19; and in addition, as will be seen later, the amount of the slowing down is close to that calculated from the proposed mechanism, so that equation (B) is still obeyed.

Equation (B) requires that  $[(1+w)/(a-1) - \ln a]$  plotted against time should give a straight line of slope  $2k_2K_0[\text{OCl}^-]_0$ . The observed values of these slopes are given in



the last column of Table I, under the heading "Slope", and in what follows when a "slope" is mentioned it is this slope that is meant. It can be seen from Table I that the slope is proportional to  $[\text{OCl}^-]_0$ , as required. For instance the following runs were done at 35° C in approximately 0.1 M potassium hydroxide:

Run	Slope, $\times 10^{-3}$	$[\text{OCl}^-]_0$ , $\times 10^{-4}$ M	Slope/ $[\text{OCl}^-]_0$ , $\times 10^{-4}$
1	6.8	100	6.8
2	6.9	100	6.9
3	7.5	100	7.5
6	1.47	20	7.35
9	11.9	200	5.95
10	0.70	10	7.0
11	3.5	50	7.0

It is also apparent that the rate is affected by the hydroxide ion concentration, and in fact it is approximately inversely proportional to the square of this concentration. Hence the quantity, slope. $[\text{OH}^-]^2/[\text{OCl}^-]_0$ , should be constant, and this is seen to be at least approximately so for the following runs, all at 35° C:

Run	$[\text{OH}^-]$ , M	Slope. $[\text{OH}^-]^2/$ $[\text{OCl}^-]_0$ , $\times 10^{-3}$	Run	$[\text{OH}^-]$ , M	Slope. $[\text{OH}^-]^2/$ $[\text{OCl}^-]_0$ , $\times 10^{-3}$
1	0.094	6.0	12	0.024	8.2
2	0.106	7.75	13	0.029	4.9
3	0.099	7.35	14	0.098	5.2
4	0.049	7.2	15	0.100	9.1
5	0.049	8.9	16	0.103	8.2
6	0.103	7.8	17	0.0995	8.3
9	0.106	6.7	18	0.0995	8.8
10	0.102	7.3	19	0.099	9.3
11	0.102	7.3	20	0.030	5.7

There is some scatter in the results, with a slight decrease in the quantity, slope. $[\text{OH}^-]^2/[\text{OCl}^-]_0$ , at low hydroxide ion concentrations. However, the general trend is clear; the average value of slope. $[\text{OH}^-]^2/[\text{OCl}^-]_0$  at 35° C is  $7.45 \times 10^{-3}$ . It will be seen that runs 15–19 with added potassium permanganate fall into line. The explanation of these results in terms of mechanism will be considered below, after noting the effect of temperature.

The runs at different temperatures give:

Run	Temp., °C	Slope. $[\text{OH}^-]^2/[\text{OCl}^-]_0$ , $\times 10^{-3}$
8	25	2.53
Mean	35	7.45
7	45	20.3

These give a good straight line for the plot of  $\log(\text{slope} \cdot [\text{OH}^-]^2/[\text{OCl}^-]_0)$  against  $1/T$ , corresponding to an activation energy of 19.6 kcal/g-molecule.

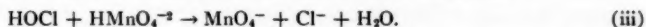
Returning to a general consideration of the mechanism, the first point to note is that in the present reaction it is the second stage that is the slower, while in the oxidation by periodate it is the first stage; at least this is true for concentrations in the region of  $10^{-4}$

to  $10^{-3}$  *M* such as were used in these experiments. This is in agreement with the activation energies for it was found (1) that the activation energy of reaction (i) is 13.9 kcal/g-molecule, while the effective activation energy for the oxidation by potassium hypochlorite is 19.6 kcal/g-molecule. This, of course, is not a simple activation energy, since equation (B) shows that

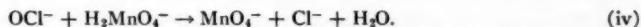
$$\text{slope. } [\text{OH}^-]^2/[\text{OCl}^-]_0 = 2K \cdot k_2[\text{OH}^-]^2$$

so that the 19.6 kcal/g-molecule should contain the heat of reaction (i) plus the activation energy of reaction (ii). Carrington and Symonds (2) give  $\Delta H$  for reaction (i) as 5.5 kcal, which makes the activation energy for reaction (ii) only 14.1 kcal. However, these conclusions ignore the question of the effect of potassium hydroxide, which must now be considered.

Higher concentrations of potassium hydroxide retard the reaction. It is not at present possible to explain this in terms of mechanism with any certainty, since more than one mechanism could give the observed fact that the rate is inversely proportional to the square of the potassium hydroxide concentration. Presumably this dependence means that hydrolyzed species, such as hypochlorous acid or  $\text{HMnO}_4^{-2}$  ions, are reacting in the rate-determining step; and that two hydrogen ions have combined with the hypomanganate or hypochlorite ions. These two hydrogen ions could go one each on the hypomanganate and hypochlorite ions, in which case the reaction would be



Alternatively both hydrogen ions might be attached to the hypomanganate ion, when the reaction would be



The hydrolysis constant of hypochlorite ions is  $5.5 \times 10^{-7}$  at  $35^\circ \text{C}$  (4). The hydrolysis constant of hypomanganate ions is unknown, but they are probably more easily hydrolyzed than manganate ions. It was found in the study of the reaction between manganate and periodate ions that the results could be explained if the second ionization constant of manganic acid is about  $7 \times 10^{-11}$ . Therefore it is probable that hypomanganate ions are more easily hydrolyzed than hypochlorite ions, and this would on the whole make reaction (iv) a little more probable. It is possible to suggest simple mechanisms for both reactions (iii) and (iv), in terms of either electron or hydrogen atom transfer, so that on this score there is nothing to choose between them.

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# FREE RADICALS BY MASS SPECTROMETRY

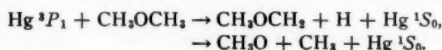
## XXII. PRIMARY DECOMPOSITION STEPS IN THE MERCURY-PHOTOSENSITIZED DECOMPOSITION OF METHANOL AND DIMETHYL ETHER<sup>1</sup>

R. F. POTTIE,<sup>2</sup> A. G. HARRISON,<sup>3</sup> AND F. P. LOSSING

### ABSTRACT

The Hg <sup>3</sup>P<sub>1</sub> photosensitized decomposition of methanol at low pressures proceeds mainly by a dissociation into CH<sub>2</sub>O radicals and H atoms. No formation of CH<sub>2</sub>OH radicals is observed. A subsidiary reaction to form CH<sub>3</sub> and OH may also be a primary step. Formation of CH<sub>2</sub>OH radicals at higher pressures is attributed to an abstraction reaction of CH<sub>3</sub>O with CH<sub>2</sub>OH.

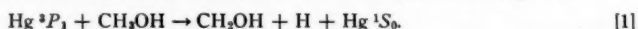
Two primary modes of dissociation are found to occur for dimethyl ether:



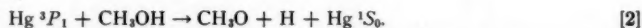
The relative probabilities of occurrence at low pressures are ~45% and ~50%, respectively. The possibility that the second reaction proceeds by formation of an excited molecule is discussed.

### INTRODUCTION

The mercury-photosensitized decomposition of methanol has been examined in some detail by Phibbs and Darwent (1) over a pressure range from 30 to 100 mm Hg and from 25° C to 500° C. They found the products of the reaction below 400° to be almost entirely hydrogen and ethylene glycol, and concluded that the primary step was

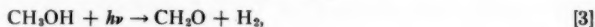


From experiments with CH<sub>3</sub>OD, they concluded that the alternative primary reaction to form CH<sub>2</sub>O did not occur,



At temperatures above 400° C CH<sub>2</sub>O and CO were formed in addition, evidently by dissociation of the radical formed in the primary step.

The direct photolysis of methanol was recently investigated by Porter and Noyes (2) using λ 1800–2000. They found that two primary steps occurred:



Since it had been shown that CH<sub>3</sub>O radicals abstract H atoms rapidly (3), they pointed out that formation of CH<sub>3</sub>O radicals by [4] would be followed by an abstraction reaction,



in which CH<sub>2</sub>OH radicals would be produced. Using CD<sub>3</sub>OH they found no formation of D<sub>2</sub> except at high conversions, and concluded that the evidence against a split into CH<sub>2</sub>OH + H in the direct photolysis was fairly strong.

It appeared, therefore, that a re-examination of the mercury-photosensitized reaction of methanol at low pressures under conditions where the occurrence of reaction [5] would be negligibly slow might provide further evidence as to the relative probabilities of the primary reactions [1] and [2].

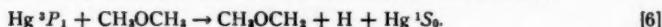
<sup>1</sup>Manuscript received September 16, 1960.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 6061.

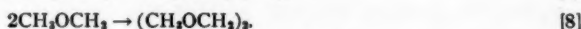
<sup>2</sup>National Research Council Postdoctorate Fellow 1958–60.

<sup>3</sup>National Research Council Postdoctorate Fellow 1957–59.

The mercury-photosensitized decomposition of dimethyl ether has been examined by Marcus, Darwent, and Steacie (4), who found the main products at 25° C to be hydrogen and 1,2-dimethoxyethane, corresponding to the primary decomposition step,



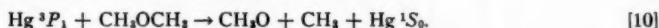
Subsequent reactions were



At 265° C products corresponding to the decomposition of the  $\text{CH}_3\text{OCH}_2$  radical were found,



They found no evidence for the formation of excited molecules in this reaction, and no evidence for a primary rupture of the C—O bond,



#### EXPERIMENTAL

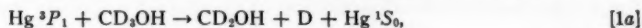
The mercury-photosensitized reactions were examined using a fast-flow system coupled to a mass spectrometer, the apparatus and method of operation being the same as that employed earlier (5, 6). In this apparatus the reactant and mercury vapor at partial pressures of a few microns are carried in a stream of helium at 8 mm pressure through a tubular reactor which is strongly illuminated by a low-pressure lamp of high intensity. The reactor is maintained at 55° C. The residence time in the illuminated zone is about 0.001 second. Directly following the illuminated zone the reaction stream passes over a small orifice through which a portion flows directly into the ionization chamber of a mass spectrometer. The bulk of the stream passes into a fast-pumping system. As discussed earlier (6), the reaction conditions resemble those of flash photolysis, in as much as radical-radical reactions are greatly favored over radical-substrate reactions.

The sample of  $\text{CD}_3\text{OH}$  was obtained from Merck and Co., Montreal. The isotopic purity was greater than 99%.

#### RESULTS AND DISCUSSION

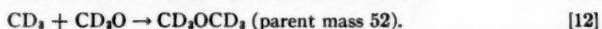
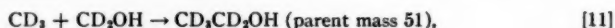
##### Methanol

In preliminary experiments on methanol, it was found that although products such as  $\text{CH}_2\text{O}$ , CO,  $\text{CH}_4$ ,  $\text{H}_2$ , and methyl radicals could be easily detected, no increase in the 31 peak attributable to the  $\text{CH}_3\text{O}$  or  $\text{CH}_2\text{OH}$  radicals could be found. It was concluded therefore that the sensitivity of the mass spectrometer to radicals of this type was quite low, and that a distinction between reactions [1] and [2] could not be made by identifying by mass the radicals produced in the decomposition of  $\text{CD}_3\text{OH}$ :



An alternative means for identifying the radicals, which had earlier been found useful (7), was employed. The addition of a small partial pressure of  $\text{Hg}(\text{CH}_3)_2$  to the reaction stream resulted, by the mercury-photosensitized decomposition of the dimethyl mercury, in the production of methyl radicals. The combination of these with radicals formed in the primary decomposition of the compound under examination then resulted in the formation of identifiable stable products. In the case of methanol it was advantageous

to employ  $\text{CD}_3\text{OH}$  instead of  $\text{CH}_3\text{OH}$ , and to add  $\text{CD}_3$  radicals by the use of  $\text{Hg}(\text{CD}_3)_2$ . Assuming that both primary steps [1a] and [2a] were occurring, the two combination reactions of  $\text{CD}_3$  radicals would be



Since ethanol and dimethyl ether have large parent peaks, the identification of the combination product by mass number was quite straightforward. As shown in Fig. 1,

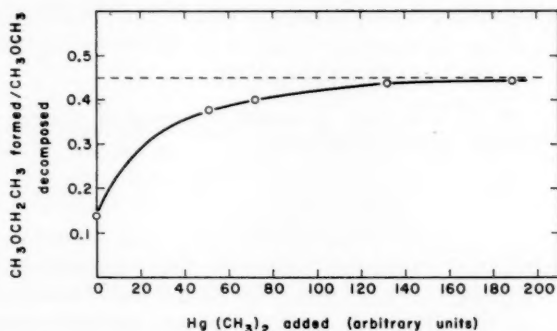
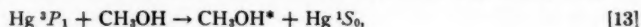


FIG. 1. Yield of  $\text{CH}_3\text{OCH}_2\text{CH}_3$  formed by reaction of the  $\text{CH}_3\text{OCH}_2$  radicals produced in primary decomposition of dimethyl ether with excess  $\text{CH}_3$  radicals from added  $\text{Hg}(\text{CH}_3)_2$ .

only  $\text{CD}_3\text{OCD}_3$  was produced in this experiment. (Additional confirmation for the identity of  $\text{CD}_3\text{OCD}_3$  is provided by the ratio of peaks at mass 50 and 52 (2.00), which was the same as the corresponding ratio for mass 45/46 in  $\text{CH}_3\text{OCH}_3$  (2.09).) After correction of the mass 51 peak height in the spectrum in Table I, the net  $\text{CD}_3\text{CD}_2\text{OH}$  peak is less than 1% of the  $\text{CD}_3\text{OCD}_3$  peak. Since the parent peak sensitivity for dimethyl ether is about three times that for ethanol, it is evident that an upper limit for  $\text{CD}_3\text{CD}_2\text{OH}$  formation is 3% of the  $\text{CD}_3\text{OCD}_3$  formation. Assuming that the rates of the combination reactions [11] and [12] are not greatly different, as seems reasonable, it seems clear that under the present experimental conditions the fraction of the primary reaction leading to the formation of  $\text{CH}_2\text{OH}$  radicals is less than 3%, and that the predominating mode of dissociation is to  $\text{CH}_3\text{O}$  and  $\text{H}$ . This is in agreement with the direct photolytic result of Porter and Noyes (2).

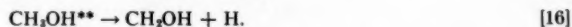
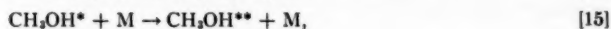
It is probable that the apparent contradiction between the present work and that of Phibbs and Darwent (1) concerning  $\text{CH}_2\text{OH}$  formation arises from the fact that the present work was carried out at very low partial pressures of methanol. This difference in conditions could affect the result in two ways. The first is the possibility that  $\text{CH}_3\text{O}$  formation results from dissociation of an excited molecule produced in a primary step,



which is deactivated at high pressures, while  $\text{CH}_2\text{OH}$  results from direct removal of a H-atom by the excited mercury atom. This explanation is quite unsatisfactory, however. If one accepts the present result that reaction [1] has a cross section less than 3% of that for reaction [2], this explanation would require the quantum yield of  $\text{H}_2$  (or other products) at high pressures to be less than 0.03. Since Phibbs and Darwent found the quantum yield of  $\text{H}_2$  to be 0.43 under their conditions, this possibility can be ruled



out. To be consistent with this observation it would be necessary to postulate two excited states, one leading to the other by collision. Following reaction [13] one would require



It seems more probable, however, that the apparent discrepancy arises from the rapid conversion of  $\text{CH}_3\text{O}$  into  $\text{CH}_2\text{OH}$  by reaction [5] as pointed out by Porter and Noyes (2). This reaction is exothermic by 7–8 kcal/mole (8), and at the pressures employed by Phibbs and Darwent it is quite possible that it would be much faster than the alternative reactions of  $\text{CH}_3\text{O}$ :



Reaction [17] appears in any case to be quite slow. No formation of dimethyl peroxide was observed by Wijnen (3) in the photolysis of methyl acetate. In an earlier paper of this series (6) the amount of dimethyl peroxide formed by [17] was found to be negligibly small under conditions favorable for its occurrence. In the present work it was not found in the experiments on  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OCH}_3$ , although  $\text{CH}_3\text{O}$  radicals were evidently present in good yields. A failure to detect dimethyl peroxide, as in Phibbs and Darwent's work, provides therefore no evidence for the absence of  $\text{CH}_3\text{O}$ . An analysis of the products from methanol photodecomposition is given in Table II. The reason

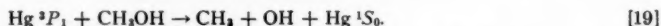
TABLE I  
Combination products in the photosensitized decomposition of  $\text{CD}_3\text{OH}$  in presence of  $\text{CD}_3$  radicals

<i>m/e</i>	Observed spectrum	$^{13}\text{C}$ isotope correction	Net spectrum of products	Parent species
52	1.00	—	1.00	$\text{CD}_3\text{OCD}_3$
51	0.05	0.044	<0.01	$\text{CD}_3\text{CD}_2\text{OH}$
50	2.00	—	2.00	—

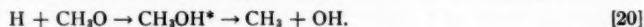
TABLE II  
Mercury-photosensitized decomposition of  $\text{CH}_3\text{OH}$  at 55° C in 8 mm helium

Species	Partial pressure ( $\mu$ )	
$\text{CH}_3\text{OH}$	Lamp off	5.01
	Lamp on	4.65
	Decomposed	0.36
$\text{CH}_3\text{OCH}_3$		0.008
$\text{CH}_2\text{O}$		0.150
$\text{CO}$		0.081
$\text{C}_2\text{H}_6$		0.010
$\text{CH}_4$		0.019
$\text{CH}_3$		0.028
$\text{H}_2\text{O}$		0.065
O balance	87%	Total $\text{CH}_3$ 0.075
C balance	85%	Total OH 0.065

for the low carbon and oxygen material balances is not apparent, since there was no visible formation of polymeric deposits in the reactor. The presence of  $C_2H_6$ ,  $CH_4$ , and  $CH_3$ , which cannot be derived from a primary split giving  $CH_3O$ , and the formation of  $H_2O$  which is evidently derived from OH radical, suggest the occurrence of a second primary decomposition,



The sum of products derived from  $CH_3$ ,  $2(C_2H_6) + (CH_4) + (CH_3OCH_3)$ , is equal to  $0.075 \mu$ , in fair agreement with the yield of  $H_2O$ , which is  $0.065 \mu$ . Reaction [19] would therefore account for about 18% of the methanol decomposed. The possibility cannot be entirely ruled out that these products result in part from an atomic cracking reaction,



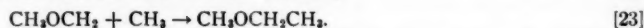
### Dimethyl Ether

Although the present results confirm the occurrence of reaction [6] as an important primary mode of dissociation of dimethyl ether, they provide strong evidence that a primary dissociation by a C—O split, reaction [10], is equally important at low pressures. An analysis of the products of the mercury-photosensitized reaction at  $55^\circ C$  in the presence of 8 mm of helium is given in Table III. The combination products  $(CH_3OCH_2)_2$ ,

TABLE III  
Mercury-photosensitized decomposition of  
 $CH_3OCH_2$  at  $55^\circ C$  in 8 mm helium

Species	Partial pressure ( $\mu$ )	
$CH_3OCH_2$	Lamp off	10.84
	Lamp on	10.35
	Decomposed	0.49
$(CH_3OCH_2)_2$		0.025
$CH_3OCH_2OCH_3$		0.016
$CH_3OCH_2CH_3$		0.070
$CH_3OH$		0.094
$CH_3O$		0.144
CO		0.076
$C_2H_6$		0.057
$CH_4$		0.057
$CH_3$		0.086
O balance	95.1%	
C balance	94.8%	

$CH_3OCH_2OCH_3$ , and  $CH_3OCH_2CH_3$  were identified by comparison of the spectra with those of pure samples of these compounds examined in separate experiments. These three products were evidently formed from  $CH_3OCH_2$  radicals by the combination reactions:



Taken together the quantities of these three products correspond to  $0.136 \mu$  of  $CH_3OCH_2$  radical, that is, 27.8% of the dimethyl ether decomposed. Since some  $CH_3OCH_2$  radicals may decompose (see below), this figure is evidently a lower limit for their formation.

A more reliable estimate for the relative probability of reaction [6] was obtained by

measuring the yield of  $\text{CH}_3\text{OCH}_2\text{CH}_3$  in the presence of methyl radicals added to the reaction stream. It can be seen from Fig. 1 that this yield reached a limiting value of 0.45 in the presence of a large excess of methyl radicals. An almost identical limit was obtained for the yield of  $\text{CH}_3\text{OCH}_2\text{CD}_3$  when  $\text{CD}_3$  radicals were added (Fig. 2). This limit must correspond quite closely to the relative probability of reaction [6].

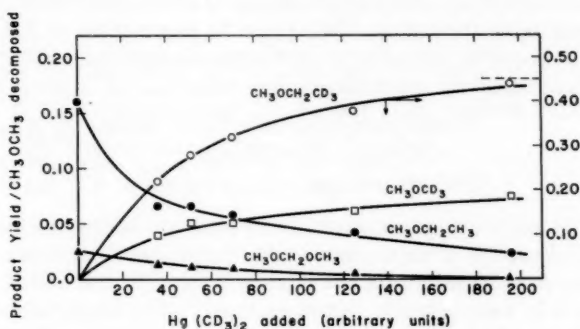
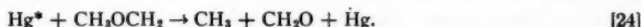


FIG. 2. Yields of products formed by radical interaction in the dimethyl ether decomposition in the presence of added  $\text{CD}_3$  radicals.

The difference between the yield of 0.45 and the yield of 0.28 as a lower limit obtained from the data in Table III must represent  $\text{CH}_3\text{OCH}_2$  radicals which are formed, but which, in the absence of excess  $\text{CH}_3$  radicals, do not appear as dimeric products. Since the radical appears to be thermally stable at  $55^\circ\text{C}$  (4) it must disappear mainly by reaction with an excited mercury atom,



The extent of this reaction is equivalent to  $0.49 (0.45 - 0.28) = 0.084 \mu$  of  $\text{CH}_3\text{OCH}_2$  radical.

From the data in Table III the relative probability of the primary reaction [10] can be estimated in two ways: from products derived from  $\text{CH}_3$ , and from products derived from  $\text{CH}_3\text{O}$ .

(a) Reactions removing  $\text{CH}_3$  radicals would be reaction [23], and the following:

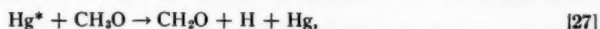


The total amount of products derived from  $\text{CH}_3$  is then, from Table III,

$$(\text{CH}_3\text{OCH}_2\text{CH}_3) + 2(\text{C}_2\text{H}_6) + (\text{CH}_4) + (\text{CH}_3) = 0.327 \mu.$$

To obtain the amount of  $\text{CH}_3$  formed in reaction [10] one must subtract  $0.084 \mu$  of  $\text{CH}_3$  produced by [24]. On this basis the relative probability of reaction [10] is  $0.243 \mu / 0.49 \mu = 0.49$ .

(b) Reactions removing  $\text{CH}_3\text{O}$  radicals would be [18], [22], [26], and the following:



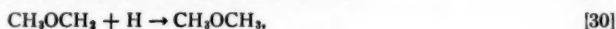
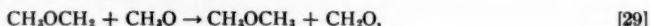
The CO found was most probably formed from  $\text{CH}_2\text{O}$  by reaction with an excited

mercury atom, since this reaction has a large relative cross section (9). The quantity of products derived from  $\text{CH}_3\text{O}$  is therefore

$$(\text{CH}_3\text{OCH}_2\text{OCH}_3) + (\text{CH}_3\text{OH}) + (\text{CH}_2\text{O}) + (\text{CO}) - (\text{CH}_2\text{O from [24]}) = 0.246 \mu.$$

This corresponds to a relative probability of 0.50<sub>2</sub> for the primary reaction [10], in good agreement with the value obtained from the yield of methyl. Although these two estimates for reaction [10] are independent of one another, their close agreement arises from the near equality of the carbon and oxygen balances given in Table III.

These estimates should be regarded as only approximate, since some re-formation of dimethyl ether may occur by the following reactions:

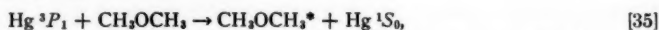


In the experiment in which a large excess of  $\text{CD}_3$  radicals was added, the yield of  $\text{CH}_3\text{OCD}_3$  amounted to only about 7% of the dimethyl ether decomposed, as shown in Fig. 2. When no methyl radicals were added as for the data in Table III, the extent of reaction [31] would be considerably less, certainly not more than 2-3%. Since the concentrations of  $\text{CH}_3\text{OCH}_2$ ,  $\text{CH}_3\text{O}$ , and  $\text{H}$  were of the same order or less than  $\text{CH}_3$ , interference by reactions [29] and [30] would also be small. Moreover it should be noted that the same limit for  $\text{CH}_3\text{OCH}_2$  production was reached by  $\text{CH}_3$  addition and by  $\text{CD}_3$  addition, even though in the latter experiment reaction [31] would not interfere with the measurement of the amount of  $\text{CH}_3\text{OCH}_3$  decomposed. This also indicates that the limits of 0.45 and 0.50 for reactions [6] and [10] are not seriously in error as a result of interference by back reactions.

Some question may be raised as to whether some or all of the  $\text{CH}_3\text{O}$  formation observed at these low pressures results from an atomic cracking reaction rather than from a primary dissociation. The following series of reactions could be proposed to explain the formation of  $\text{CH}_3\text{O}$  at low pressures and its absence under the higher pressure conditions of Marcus, Darwent, and Steacie (4):



The results given in Figs. 1 and 2 show, however, that this series of reactions does not play a significant role under the present conditions. As shown in Fig. 1, the addition of an excess of  $\text{CH}_3$  radicals, which would suppress reaction [32], gives an upper limit of 0.45 for the relative probability of reaction [6], and not nearly unity as would be the case if reaction [6] were the only primary mode of decomposition. The yield of  $\text{CH}_3\text{OCH}_2\text{CD}_3$  in Fig. 2 confirms this observation. Moreover, the yield of  $\text{CH}_3\text{OCD}_3$  (Fig. 2) does not pass through a maximum and then decrease with increasing  $\text{CD}_3$  addition as would be expected if reactions [32] and [33] were important under these conditions. It seems quite clear from these results that at low pressures  $\text{CH}_3\text{O}$  is formed in a primary decomposition step with a probability of about 0.50. The non-occurrence of this mode of dissociation at pressures in the 28- to 500-mm region (4) suggests that it may go by formation of an excited molecule,



followed by the dissociation and deactivation reactions [33] and [34]. Since the 8 mm

of helium used in the present experiments would be completely ineffective in quenching excited molecules, the effective pressure is that of the ether itself, i.e. about 0.010 mm, and deactivation would be quite slow. Even in the experiments in which methyl radicals were added, the total partial pressure effective for deactivation was still well below 0.05 mm.

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## EXCEPTIONS TO HUDSON'S RULES OF ISOROTATION

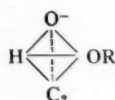
### THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF ANOMERIC PYRIMIDINE 2-DEOXY-D-RIBONUCLEOSIDES<sup>1</sup>

R. U. LEMIEUX AND M. HOFFER

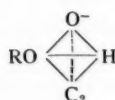
#### ABSTRACT

Nuclear magnetic resonance spectroscopy and optical rotatory dispersion measurements were used to correlate the configurations of anomeric pairs for the 1-(2-deoxy-D-ribofuranosyl) derivatives of 5-methyl- and 5-fluoro-uracil. The optical rotations of the anomers were found opposite to those expected on the basis of Hudson's rules of isorotation.

Hudson's rules of isorotation in their earliest form (1) in effect stated that for D-glycosides the more dextrorotatory (or less levorotatory) anomer is to be named  $\alpha$ -D-. As evidence for the absolute configurations of glycopyranosides accumulated, it became evident that the rules correlate rotation and anomeric configuration (2). It has consequently become a widespread practice to assign absolute anomeric configurations on the basis of Hudson's rules and the assumption that the absolute configurations are those which follow.



$\alpha$ -D or  $\beta$ -L



$\beta$ -D or  $\alpha$ -L

The purpose of this communication is to report that the rules of isorotation are violated in every respect in the case of certain 2-deoxy-D-ribonucleosides. Thus, although the rules are well tested and are undoubtedly of value in assigning anomeric configurations to O-glycopyranosyl compounds, reserve is indicated in their application to the kinds of glycosides for which there exists no compelling empirical evidence (3).

Hoffer, Duschinsky, Fox, and Young (4) recently have reported syntheses of the anomeric pairs for the pyrimidine 2-deoxy-D-ribonucleosides I and II, and III and IV (see Fig. 3). The optical rotations for these compounds measured with the *D*-line of sodium are presented in Table I.

On the basis of the anomeric configurations assigned to the compounds in Table I, except for the anomers V and VI and the anomers I and II the rotations for these compounds when measured in dimethylformamide are opposite to those required by Hudson's rules. The assignments of configuration are those made by Hoffer and co-workers (4) on the basis of the fact that all the natural 2-deoxyribonucleosides possess the  $\beta$ -D-configuration (5) and the assumption that the anomers obtained in the greater yield, in their syntheses (4) from crystalline 3,5-di-*O*-*p*-toluyl-2-deoxy-D-ribofuranosyl chloride, are configurationally related.

Application of Hudson's rules to isomeric glycosyl compounds of course requires that the compounds differ only in the configuration of the anomeric center. Hoffer (6) has shown, in this respect, that methylation of compounds V and VI introduces a methyl

<sup>1</sup>Manuscript received September 1, 1960.

Contribution from the Department of Chemistry, University of Ottawa (R.U.L.), Ottawa, Ontario, and Hoffmann-LaRoche, Inc. (M.H.).

TABLE I  
Optical rotations of pyrimidine 2-deoxy-D-ribonucleosides.

Compound	$[\alpha]_D$	Solvent ( $c$ , 2)
1. 1-(2-Deoxy- $\alpha$ -D-ribofuranosyl)-5-methyluracil (I)	+7.2° +13 +46.6	Water N Sodium hydroxide Dimethylformamide
2. 1-(2-Deoxy- $\beta$ -D-ribofuranosyl)-5-methyluracil (II) (thymidine)	+20 +32.8* +15.1	Water N Sodium hydroxide Dimethylformamide
3. 1-(2-Deoxy- $\alpha$ -D-ribofuranosyl)-5-fluorouracil (III)	-21 +20.5	Water Dimethylformide
4. 1-(2-Deoxy- $\beta$ -D-ribofuranosyl)-5-fluorouracil (IV)	+37 +48.6	Water Dimethylformamide
5. 3,5-Di- <i>O-p</i> -toluyl I (V)	-14.5 -20.4	Pyridine Dimethylformamide
6. 3,5-Di- <i>O-p</i> -toluyl II (VI)	-50 -36.5	Pyridine Dimethylformamide
7. 3,5-Di- <i>O-p</i> -toluyl III (VII)	-72.5 -69.2	Pyridine Dimethylformamide
8. 3,5-Di- <i>O-p</i> -toluyl IV (VIII)	-17 -4	Pyridine Dimethylformamide

\*P. A. Levene and E. S. London. J. Biol. Chem. **83**, 793 (1929); see also X. Schindler. Helv. Chim. Acta, **32**, 979 (1949).

group in each case at position-3 of the pyrimidine ring. Thus, in view of the synthesis of V and VI from pure 3,5-di-*O-p*-toluyl-2-deoxy-D-ribofuranosyl chloride (4), there can be no doubt that I and II are truly anomeric. The ultraviolet absorption spectral data obtained with solutions of III and IV as well as I and II at varying pH also provided evidence for the anomeric relationship between the fluorides III and IV (6). As will be seen below, the nuclear magnetic resonance spectra and optical rotatory dispersion curves for these compounds confirm these conclusions.

Lemieux, Kullnig, Bernstein, and Schneider (7) have shown that the anomeric configurations of aldoses in principle often can be determined by proton magnetic resonance spectroscopy. The application usually requires detection of the fine structure for the signal of the anomeric hydrogen and a knowledge of the conformation of the compound. It is clear, however, that unless changes in the aglycon of a glycoside change the conformation of the sugar residue, then the fine structure of the signals for the protons of the sugar residue should not be altered appreciably. Also, the chemical shifts can be expected to be relatively constant. Certainly, when the fine structure and chemical shifts are substantially the same for the protons in the sugar portions of two glycosides differing only in the aglycon, the two compounds must possess the same anomeric configurations. Thus, proton magnetic resonance spectroscopy should be useful for classifying anomeric compounds even in the absence of a knowledge of their configurations.

The proton magnetic resonance spectra for the nucleosides listed in Table I are given in Figs. 1 and 2. The signals in the spectra can be readily assigned to the hydrogens in the compounds on the basis of the experience with related compounds (7, 8) but these assignments are not needed for the present purpose of grouping the compounds into two series of configurationally related substances—a feat which is not possible on the basis of optical rotations measured at the *D*-line of sodium only. However, as seen in Fig. 3, the optical rotatory dispersion curves for compounds I to IV clearly indicate the configurational relationships at the anomeric centers for these compounds. That is, it must

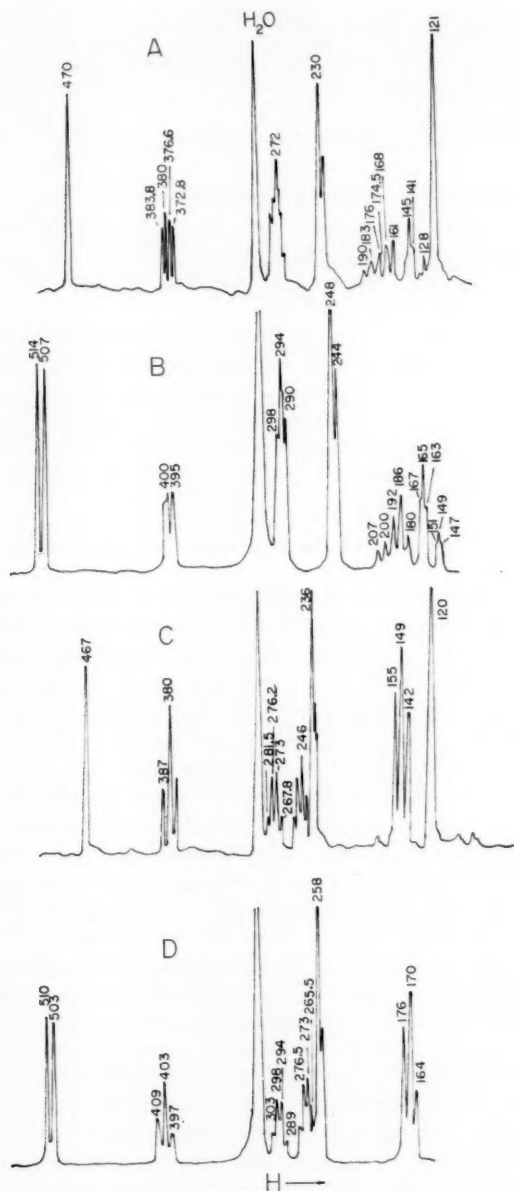


FIG. 1. The nuclear magnetic resonance spectra of anomeric glycofuranosides measured in deuterium oxide with a high-resolution Varian spectrometer operating at 60 Mc/sec. The positions of the signals are from tetramethylsilane used as an external standard.

- (A) 1-(2-Deoxy- $\alpha$ -D-ribofuranosyl)-5-methyluracil (I).
- (B) 1-(2-Deoxy- $\alpha$ -D-ribofuranosyl)-5-fluorouracil (II).
- (C) 1-(2-Deoxy- $\beta$ -D-ribofuranosyl)-5-methyluracil (III).
- (D) 1-(2-Deoxy- $\beta$ -D-ribofuranosyl)-5-fluorouracil (IV).

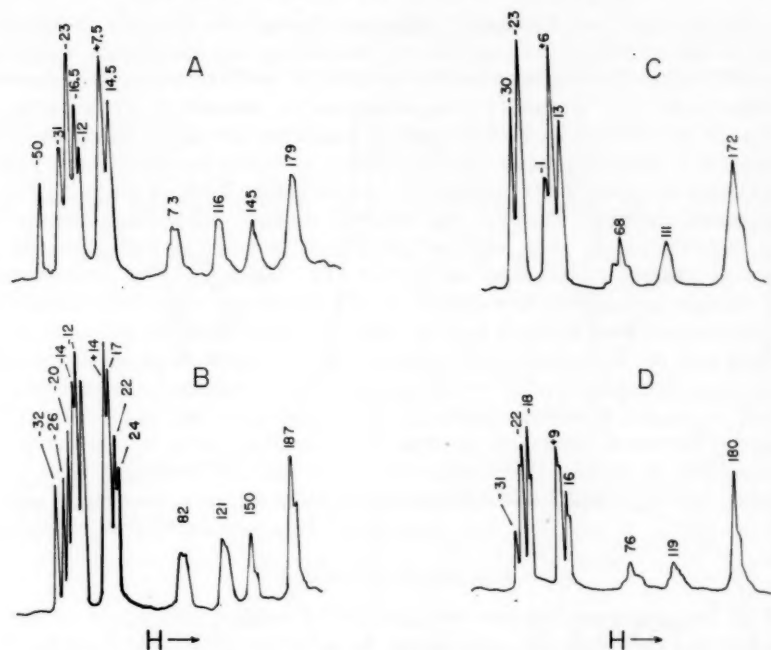


FIG. 2. The nuclear magnetic resonance spectra of anomeric glycofuranosides measured in dimethyl sulphoxide with a high-resolution Varian spectrometer operating at 60 Mc/sec. The positions of the signals are from chloroform used as an external standard. The signals at higher field were obscured by those of the solvent.

- (A) 1-(Di-*O-p*-toluyl-2-deoxy- $\alpha$ -D-ribofuranosyl)-5-methyluracil (V).
- (B) 1-(Di-*O-p*-toluyl-2-deoxy- $\alpha$ -D-ribofuranosyl)-5-fluorouracil (VII).
- (C) 1-(Di-*O-p*-toluyl-2-deoxy- $\beta$ -D-ribofuranosyl)-5-methyluracil (VI).
- (D) 1-(Di-*O-p*-toluyl-2-deoxy- $\beta$ -D-ribofuranosyl)-5-fluorouracil (VIII).

be expected (9) that for such closely related substances, the two compounds whose specific rotations follow similar trends with decreasing wavelength are configurationally related. These results show clearly that the anomalous rotations (from the viewpoint of Hudson's rules and the assigned configurations (4)) obtained with the *D*-line of sodium are not the result of a fortuitous crossing-over of the rotatory dispersion curves but, instead, that the anomalous rotations are a characteristic of the compounds at all the wavelengths used.

Thus, the nuclear magnetic resonance spectra and optical rotatory dispersion curves leave no doubt as to which of the compounds (I to IV) are configurationally related. The conclusion that the rotations of these compounds do not agree with predictions based on Hudson's rules of course requires unequivocal proof of the absolute configuration of at least one of the compounds. Michelson and Todd (5) have established the configuration of thymidine (I). As indicated above synthetic evidence already exists for the configurations and structures depicted in Fig. 3 for compounds II, III, and IV. It was also found possible to deduce the configurations and conformations of thymidine (I) and its anomer (II) from their nuclear magnetic spectra and the range of coupling constants calculated by Karplus (10) for two protons on neighboring saturated carbons. A detailed consideration of these matters is reserved for a separate report (11).

## Rotatory Dispersion Curves

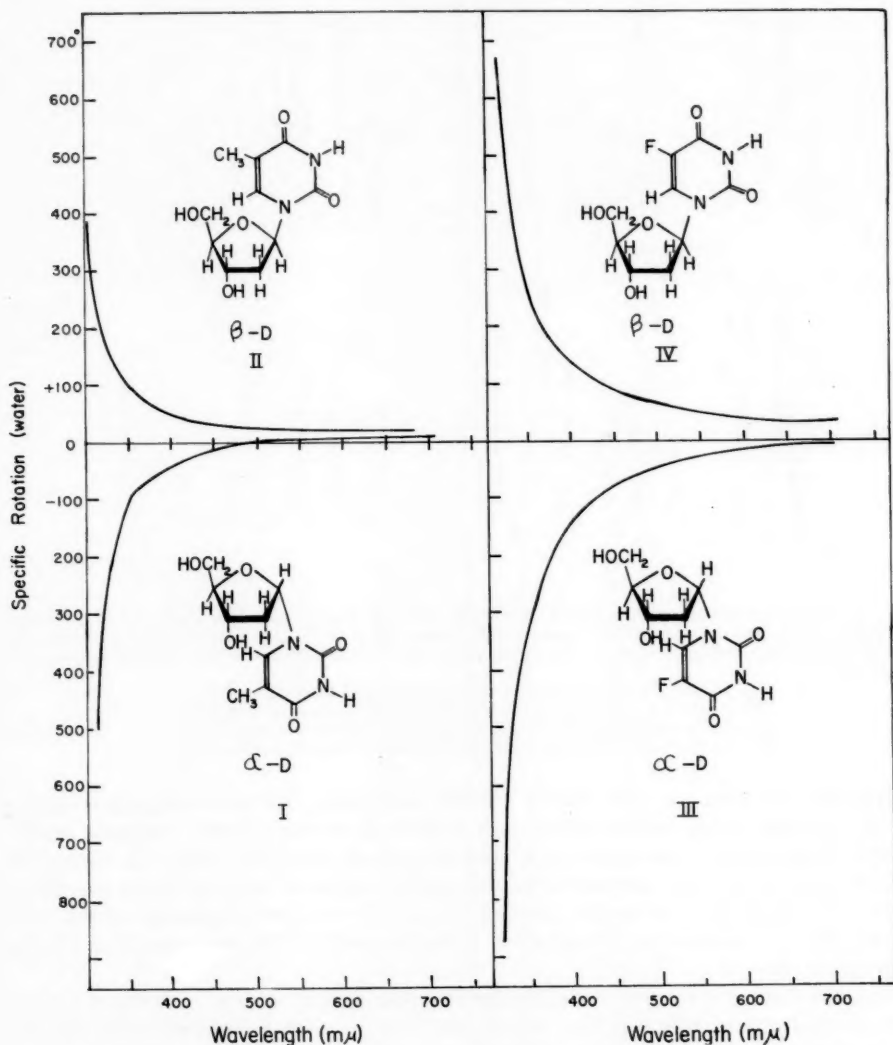


FIG. 3. Optical rotatory dispersion curves of the indicated compounds measured, using about 0.75% solutions in water, at 24–25°.

Fox (12) has already anticipated the failure of Hudson's rule<sup>7</sup> of isotrotation in the series of pyrimidine nucleosides. Evidence has been obtained (13) that the rotations of 2-deoxyglucopyranosides and 2-deoxyribosepyranosides follow Hudson's rules. Indications that this may not have been the case was suggested by the rotations observed (14) for 2-deoxy-D-glucose tetraacetates. The so-called  $\alpha$ -D- ( $[\alpha]_D +12.3^\circ$  (ethanol)) and  $\beta$ -D- compounds ( $[\alpha]_D^{20} +30^\circ$  (ethanol)) were found (13) to be both impure preparations of 2-deoxy- $\beta$ -D-glucopyranose tetraacetate.



In conclusion, the configurations of thymidine (I) and its  $\alpha$ -anomer (II) are opposite to those which would have been anticipated on the basis of Hudson's rules of isorotation and the rotations measured either in water or aqueous sodium hydroxide. The rotations of the compounds are, however, in accordance with Hudson's rules when measured in dimethylformamide as are the rotations of their di-*O*-toluyl derivatives V and VI, respectively, when measured either in pyridine or dimethylformamide. The substitution of the methyl group in the thymine residue by fluorine atom results in compounds, III and IV, whose rotations are opposite to those expected from Hudson's isorotation rules when measured either in water or dimethylformamide. Also, the rotations of the di-*O*-toluyl derivatives of III and IV (VII and VIII, respectively) are not in agreement with Hudson's rules when measured either in pyridine or dimethylformamide. Thus, it is evident that the precise meaning of the  $\alpha$ - and  $\beta$ -designations which are used to describe carbohydrate structures needs revision. The convention, as was seen above, used in carbohydrate nomenclature which employs two different designations to represent each of the two absolute configurations for anomeric centers is unique in the field of organic chemistry. It seems reasonable in view of the above described exceptions to Hudson's rules of isorotation that serious consideration be given to a substitution of these rules of nomenclature by rules that are more compatible with the more widely accepted procedures for naming such structures.

#### ACKNOWLEDGMENTS

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# THE CONFIGURATION AND CONFORMATION OF THYMIDINE<sup>1</sup>

R. U. LEMIEUX

## ABSTRACT

The nuclear magnetic resonance spectrum for the anomer of the naturally occurring deoxyribonucleoside thymidine allowed a conclusion as to its anomeric configuration through an interpretation of the fine structure observed in the signals for the  $H_1'$ ,  $H_2'$ , and  $H_2''$  atoms. Thus, indirect evidence for the configuration of thymidine was obtained. The nuclear magnetic resonance spectrum of thymidine suggests that the compound possesses considerable conformational purity when dissolved in water since an interpretation of the spectrum leads to the assignment of the plausible conformation wherein all of the large substituents on the furanose ring are in partially staggered orientations with the neighboring atoms.

The anomeric configuration of thymidine has been established beyond any reasonable doubt by Michelson and Todd (1). A purpose of this communication is to show that it is possible to arrive at the same conclusion by a consideration of the nuclear magnetic resonance spectra for thymidine and its  $\alpha$ -anomer (2, 3). More important, the results of the present investigation allow conclusions as to the conformation of thymidine in aqueous solution.

It was not possible to establish the configuration of thymidine directly from its N.M.R. spectrum (see Fig. 1) since there proved to be little, if any, chemical shift between the 2-hydrogens ( $H_2'$  and  $H_2''$ ). For this reason, the signal of the 1-hydrogen ( $H_1'$ ) was found to be in the form of a triplet, the spacing ( $7.0 \pm 0.2$  c.p.s.) of which reflects the

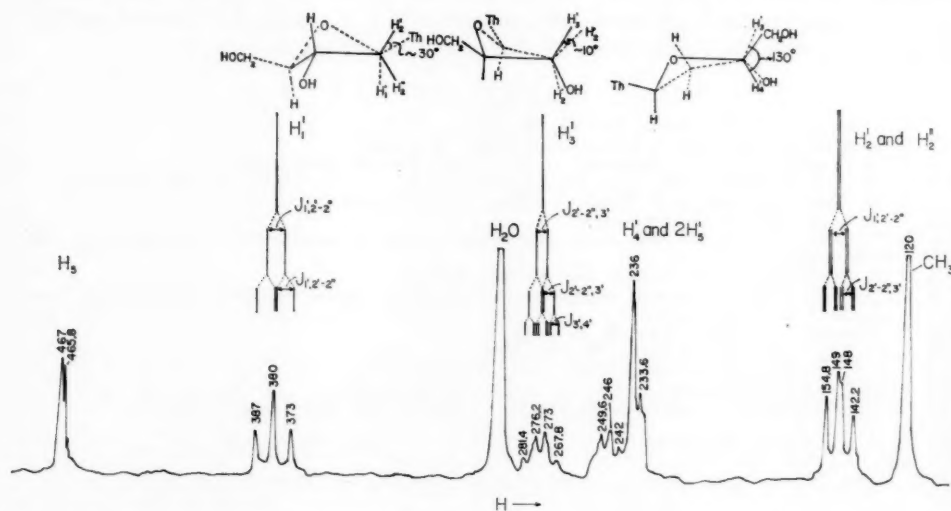


FIG. 1. The experimental and calculated nuclear magnetic resonance spectra of thymidine. The spectrum was measured using a 20% solution in deuterium oxide at 25° with a high-resolution spectrometer operating at 60 Mc/sec. The positions of the signals are from tetramethylsilane used as an external standard. The projection formulas represent the conformation for thymidine suggested by the spectrum. The projections are those obtained by viewing the molecular model first along the  $C_2$  to  $C_1$  bond with  $C_3$  in front, secondly along the  $C_3$  to  $C_2$  bond with  $C_4$  in front, and thirdly along the  $C_4$  to  $C_3$  bond with  $C_1$  in front.

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

average of the coupling with  $H_2'$  and  $H_2''$  (4). The magnitude of the coupling requires that  $H_1'$  be coupled strongly ( $J > 5$  c.p.s.) with  $H_2'$ , since the coupling of  $H_1'$  with  $H_2''$  should not be greater than 9. In view of the dependency of the coupling between neighboring hydrogens on their spatial arrangement relative to the bridging carbons (5, 6) and the fact that  $H_1'$  is coupled to an extent of less than 3 c.p.s. with  $H_2'$  in pyrimidine ribonucleosides (7), it is apparent that the pyrimidine deoxyribonucleosides and the pyrimidine ribonucleosides possess *different* conformations for the furanose rings.

The N.M.R. spectrum for the anomer of thymidine (Fig. 2) which was recently

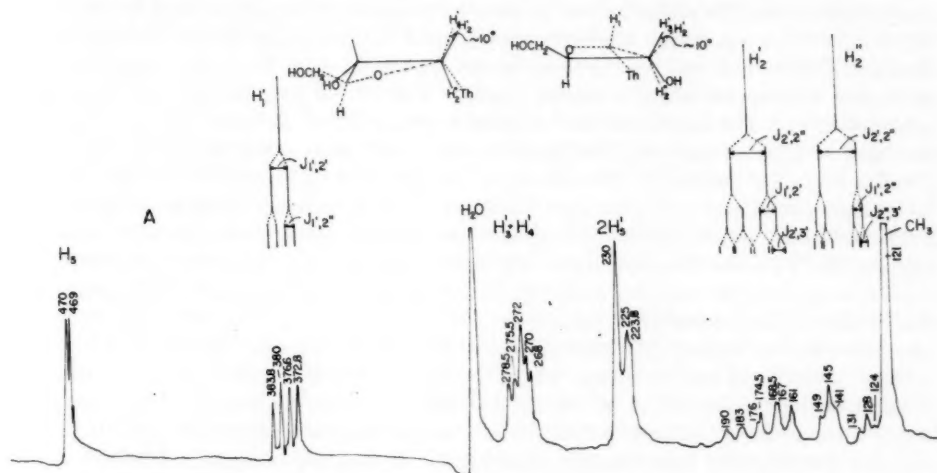


FIG. 2. The experimental and calculated nuclear magnetic resonance spectra of the  $\alpha$ -anomer of thymidine. The spectrum was measured using a 20% solution in deuterium oxide at 25° with a high-resolution spectrometer operating at 60 Mc/sec. The positions of the signals are from tetramethylsilane used as an external standard. The projection formulas are to be interpreted as is indicated in Fig. 1 for the  $\beta$ -anomer and represent the conformation for the compound suggested by the spectrum.

synthesized by Hoffer and co-workers (3) provides evidence for its configuration and, consequently, an indirect proof for the configuration of thymidine. Also, the spectrum for thymidine (Fig. 1) allows a conclusion as to the conformation of the compound. The procedure used is based on two assumptions which must be recognized. First of all, the procedure requires the assumption that the compounds are conformationally pure under the conditions that their spectra were measured, namely, in a 20% solution in deuterium oxide at 25°. Secondly, it must be assumed that the variation in the coupling between neighboring hydrogens calculated by Karplus (6) exists for the type of structure under consideration with sufficient precision to warrant their application in this manner. It is noteworthy in this respect that the application does not require a high degree of precision. Consequently, it is felt unlikely that variations (in coupling versus projected angle) from the expected values should arise which would be sufficiently great as to be misleading. In view of these assumptions, the main justification for the approach, at this stage of the development of the nuclear magnetic resonance spectroscopy of carbohydrate structures, is the results obtained. Certainly, as will be seen in the interpretations that follow, wherever it was possible to anticipate a result the approach based on nuclear magnetic

resonance spectroscopy provided a confirmation of the expectation. Also, the conformation arrived at for thymidine is intrinsically attractive from the point of view of non-bonded interactions.

The signals for the 2-hydrogens of the anomer of thymidine (see Fig. 2) are chemically shifted by 37 c.p.s. and these (average) are shifted about 222 and 120 c.p.s. from the signals for  $H_1'$  and  $H_3'$ . Under these circumstances, the fine structures observed for signals of the  $H_1'$ ,  $H_2'$ , and  $H_2''$  atoms can be analyzed simply on the basis of first-order perturbation theory (8). The spacing of the quartet observed for the  $H_1'$  atom requires this proton to be coupled with the  $H_2'$  and  $H_2''$  atoms by amounts of  $7.2 \pm 0.2$  c.p.s. and  $3.8 \pm 0.2$  c.p.s. The signal for one of the 2-hydrogens appears as two triplets separated by 17 c.p.s. This separation infers that the carbon valence angle for the 2-hydrogens is about  $107^\circ$  (9). The spacing for both these triplets is  $4.0 \pm 0.2$  c.p.s. Therefore, the particular 2-hydrogen which is weakly coupled with  $H_1'$  is coupled to nearly the same extent with  $H_3'$ . The signal for the 2-hydrogen which occurs at lower field is *roughly* in the form of a broad quintet. This must be the 2-hydrogen which is strongly coupled,  $J = 7.2 \pm 0.2$  c.p.s., with  $H_1'$ . The spacing of the quintet requires this 2-hydrogen also to be strongly coupled,  $J = 7 \pm 0.5$  c.p.s., with  $H_3'$ . The knowledge of these coupling constants and the configuration of 2-deoxy-D-ribose together with the values calculated by Karplus (6, 7) for the dihedral angles the neighboring protons can be expected to define in order to provide the coupling observed allows the following deduction of the conformation of the synthetic anomer of thymidine. Precise atomic models of the conformational type described by Barton (10) were employed as a basis for these deductions.

For the  $H_3'$  atom to be coupled  $4.0 \pm 0.2$  c.p.s. with a 2-hydrogen, it must define a dihedral angle of either  $45$  to  $50^\circ$  or  $125$  to  $130^\circ$  with the 2-hydrogen. If  $H_3'$  projected between  $H_2'$  and  $H_2''$ , then it would define dihedral angles of  $45$  to  $50^\circ$  and  $70$  to  $75^\circ$  with the 2-hydrogens. This situation would result in coupling constants of  $3.6 \pm 0.4$  and  $0.6 \pm 0.4$  c.p.s. and, therefore, can be eliminated as a possibility. If  $H_3'$  should be sufficiently axially oriented to define a dihedral angle of  $45$  to  $50^\circ$  with  $H_2'$  and if the compound possessed the  $\beta$ -D-configuration (1,3-*trans*-configuration) (2) then  $H_1'$  would necessarily project between the hydrogens at position 2 and define dihedral angles in the range  $10$  to  $30^\circ$  with  $H_2''$  and, consequently,  $90$  to  $110^\circ$  with  $H_2'$ . Thus,  $H_1'$  would be coupled to the extents of  $6$  to  $7.6$  and  $-0.4$  to  $0.8$  c.p.s. with the hydrogens at the 2-position, coupling constants which are not in agreement with those observed ( $7.2 \pm 0.2$  and  $3.8 \pm 0.2$  c.p.s.). Consequently, the possibility that the compound exists in both this configuration and conformation can also be eliminated. In view of the fact that the configuration of a 2-deoxy-D-ribofuranoside does not allow a dihedral angle of  $125$ – $130^\circ$  to be defined by  $H_3'$  and  $H_2'$ , only one conformation remains possible on the assumption that the compound possesses the  $\beta$ -D-configuration; namely, the conformation which would have  $H_3'$  and  $H_2''$  define a dihedral angle of  $125$ – $130^\circ$ . In this conformation,  $H_1'$  would necessarily project between  $H_2'$  and  $H_2''$ . As was seen above for a similar situation, the coupling constants observed for  $H_1'$  and  $H_2'$  and for  $H_1'$  and  $H_2''$  cannot be accounted for in this event. *Therefore, the anomer of thymidine cannot possess the  $\beta$ -D-configuration.* That the compound indeed possesses the  $\alpha$ -D-configuration is supported not only by the fact that an interpretation of its spectrum is possible on the basis of this configuration but also by the fact that the interpretation places the compound in a favorable conformation.

As was seen above, the coupling constants observed for  $H_1'$  with the 2-hydrogens cannot be accounted for should  $H_1'$  project between  $H_2'$  and  $H_2''$ . Therefore, since the

anomer of thymidine has the  $\alpha$ -D-configuration, should  $H_3'$  define the rather unlikely dihedral angle of 45 to 50° with  $H_2'$ ,  $H_1'$  would define a dihedral angle of 10 to 30° with  $H_2'$  and 130 to 150° with  $H_2''$ . On this basis the coupling constants for  $H_2'$  and  $H_2''$  with  $H_3'$  would be 5.8 to 7.6 and 4.4 to 6.8 c.p.s., respectively. Although these coupling constants are reasonably close to those observed, the conformation they would imply is much less attractive than that which would have  $H_3'$  define a dihedral angle of only 5 to 10° with  $H_2'$  and, therefore, a dihedral angle of 125 to 130° with  $H_2''$ . On this basis, the coupling constants for  $H_3'$  with  $H_2'$  and  $H_2''$  would be expected to be in the ranges 7.6 to 8.2 and 3.2 to 4.0 c.p.s., respectively, as compared with the observed values of  $7 \pm 0.5$  and  $4.0 \pm 0.2$  c.p.s. It would follow that  $H_1'$  would be similarly oriented relative to  $H_2'$  and  $H_2''$ , a condition which would meet the observed coupling constants of  $7.2 \pm 0.2$  and  $3.8 \pm 0.2$  found for  $H_1'$ . Therefore, the conformation of the anomer of thymidine (1-(2-deoxy- $\alpha$ -D-ribofuranosyl)-5-methyluracil) must be that represented in Fig. 2 in which none of the substituents about the furanoside ring are eclipsed with their neighbors. Jardetzky (7) has commented on this type of conformation in relation to the conformations of ribonucleosides. It is seen that  $H_2'$  and  $H_2''$  are in "equatorial" and "axial" orientations, respectively. Therefore, it would be expected (5) that the signal for  $H_2'$  would be at lower field than that for  $H_2''$ , as is in fact the case. The first-approximation, theoretical spectrum for the compound is shown in Fig. 2. The resemblance of this spectrum to that actually determined should be noted.

The N.M.R. spectrum (see Fig. 1) of the natural 2-deoxyribonucleoside, thymidine, sheds considerable light on the conformation of this important biochemical. The average coupling of  $H_1'$  with the 2-hydrogens,  $7.0 \pm 0.2$  c.p.s., requires that  $H_1'$  define dihedral angles of about 150° and 30° with  $H_2'$  and  $H_2''$ , respectively. The structure of the signal for  $H_2'$  and  $H_2''$  requires that the average of the coupling constants of these protons with  $H_3'$  is about 5.8 c.p.s. The structure of the signal for  $H_3'$  supports this contention.

The signal in the form of a rough quartet at about 274.5 c.p.s. can be assigned to  $H_3'$ . The assignment can be made first of all on the basis that the spacing between the first and second lines of 5.2 c.p.s. is in close agreement with the coupling constant, 5.8 c.p.s., observed for the average of the coupling of the two hydrogens at the 2-position with  $H_3'$ . Secondly, the structure for the signal for the two hydrogens at position 5 at 236 c.p.s. clearly indicates that the signal for these hydrogens is not greatly chemically shifted from the signal for  $H_4'$ . However, the signal for  $H_3'$  cannot be a simple quartet but must be an octet in view of the coupling of  $H_3'$  with  $H_2'$ ,  $H_2''$ , and  $H_4'$ . As is indicated in Fig. 1, the structure of the signal can be reasonably accounted for as resulting from coupling interactions of 5.8 c.p.s. with each of the hydrogens at the 2-position and 3.2 c.p.s. with  $H_4'$ . On this basis, the conformation for thymidine which is best accommodated by the results is that depicted in Fig. 1. The geometrical and spectral features for thymidine and its  $\alpha$ -anomer are summarized in Table I. The conformation implied by the spectrum for thymidine clearly possesses a favorable disposition of the groups about the furanoside ring. It is noteworthy that thymidine possesses a conformation for the furanoside ring which closely approximates the  $C_4$  conformation for cyclopentane (11) while the conformation of the  $\alpha$ -anomer is closer to the so-called  $C_2$  conformation for cyclopentane. It is also of interest to note that the substitution of  $H_2''$  by a hydroxyl group to form a ribonucleoside would require a near eclipsing of the hydroxyl with the 3-hydroxyl. Consequently, it is not surprising that, as seen above, the conformation of the furanoside ring of thymidine is different to that of pyrimidine ribonucleosides. The general features of the N.M.R. spectrum of thymidine requires that it possess considerable conformational



TABLE I  
Conformational and N.M.R. spectral features for thymidine  
and its  $\alpha$ -anomer

Neighboring atoms	Projected angle	Spin-spin coupling constant, c.p.s.	
		Expected (6,7)	Found
1. Thymidine	$H_1', H_2''$	6.0	
	$H_1', H_2'$	6.5	
		6.3 (average)	7.0
	$H_2', H_3'$	7.5	
	$H_2'', H_3'$	3.5	
		5.5 (average)	5.8
2. $\alpha$ -Thymidine	$H_3', H_4'$	3.5	3.2
	$H_1', H_2''$	130°	3.5
	$H_1', H_2'$	10°	7.5
	$H_2', H_3'$	10°	7.5
	$H_2'', H_3'$	130°	3.5
			4.0

purity, a matter which is noteworthy in view of the role of deoxynucleosides as building units of the templates of living processes.

In conclusion, it is of interest to note that the present results provide further evidence of the fact that nuclear magnetic resonance spectroscopy can be an important tool for elucidation of the detailed structure of biochemicals in aqueous solution.

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# CHEMICAL EFFECTS OF THE $(n,\gamma)$ ACTIVATION OF BROMINE IN THE ALKYL BROMIDES: THE HALOMETHANES<sup>1</sup>

W. E. HARRIS<sup>2</sup>

## ABSTRACT

Techniques for studying the chemical effects accompanying the neutron irradiation of the halomethanes with a neutron flux of only  $10^8$  neutrons per square centimeter per second are described. Results are presented from the irradiation of mixtures of bromine with the four bromomethanes and carbon tetrachloride. The formation of organic products which occur as the result of "hot", "hot-spot diffusive", and "thermal" reactions are discussed. The amounts of products resulting from these three types of reactions are estimated. Observations with respect to the formation of bromoethanes are also discussed.

## INTRODUCTION

When a sample containing bromine atoms is irradiated with thermal neutrons, the bromine isotopes of masses 79 and 81 are converted to radioactive bromine of masses 80 and 82 by the  $(n,\gamma)$  nuclear reaction. In this transformation, the nucleus emits from two to six gamma rays in cascade. The resulting recoil momentum gives the radiobromine sufficient energy to dissociate it from the parent molecule and bring about chemical reactions with the other molecules present.

If an organic bromide is irradiated some of the radioactive bromine is converted to an inorganic form (1) and some is retained in various organic forms. The predominant organic product is usually the parent molecule in which radiobromine has been substituted for the inactive bromine, but in addition, a wide variety of new organic compounds are formed. Conversely, it has been found that when a mixture of bromine and pentane (2) or carbon tetrachloride (3) are irradiated, some of the radiobromine is converted to an organic form by recoil labelling and some remains as inorganic bromine. Thus, when a mixture of bromine and an alkyl bromide is irradiated, the bromine atoms in the organic radiobromine compounds originate from both the alkyl bromide and the bromine. Thus it appears that the initial chemical form of the bromine is of secondary importance. Reviews of the many papers in this field have been published by Willard (4, 5).

Many studies (5) have been made with the haloalkanes to determine the fraction of radiohalogen appearing in organic combination, called the organic yield, under a variety of conditions. Experiments have also determined the nature of the new organic products. The organic yield of the irradiated sample has been classically determined by extraction with an aqueous solution of reducing agent and carrier salt and counting the radioactivity of the organic and aqueous layers separately. The organic compounds have frequently been determined by addition of carriers to the extracted organic phase followed by a fractional distillation to separate the components. Evans and Willard (6) have shown that gas chromatography can be applied to the direct separation of the organic products with or without the addition of carriers.

The present work describes the results of neutron irradiation of a wide range of bromomethane-bromine mixtures. The organic yields were determined by a new technique involving reaction of the inorganic radiobromine in the gas phase with solid potassium ferrocyanide (7), and the organic products were separated by gas chromatography.

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## EXPERIMENTAL

*Sample Preparation*

In order to attain the high purity required (8, 9) for a study of hot-atom reactions, samples were purified by gas chromatography prior to irradiation. About 0.5-ml samples of reagent grade bromoalkanes were purified with a column 2.5 meters long and 2.2 cm i.d. which contained a packing of Dow-Corning high-vacuum silicone grease on firebrick. The effluent was monitored with a thermal detector which was bypassed in favor of a condenser when the desired material was eluting from the column. A central fraction was condensed and collected in the irradiation vessel which consisted of a 0.5-ml bulb blown at the end of 4-mm soft-glass tubing. The samples were cooled with liquid air, evacuated, sealed, and immediately wrapped with black electrical pressure-sensitive tape to exclude light. When desired, a measured volume of either liquid bromine or its saturated vapor was transferred to the irradiation vessel prior to the collection of the bromoalkane.

Because of the low boiling point ( $3.6^\circ$ ) of bromomethane, samples of it required special handling. Before addition to the gas chromatographic column a sample was frozen in an ampoule with liquid air. This was opened and put into a chamber at the inlet to the column where the sample evaporated into the eluent gas stream. The condenser at the outlet of the column was cooled by a stream of air precooled with liquid nitrogen. The bromomethane was collected in ampoules cooled with Dry Ice.

*Irradiation*

The samples were irradiated at ambient temperature, about  $25^\circ$ , for 10–50 hours in a special facility (7) on the external face of the shielding of the Chalk River NRX reactor. The neutron flux of this position was slightly over  $10^8$  neutrons per square centimeter per second and a measurement of the gamma flux with a portable survey meter gave a maximum reading of 11 roentgens per hour. Thus the total gamma-ray dosage was considerably less than the value of  $2 \times 10^4$  roentgens which has been shown to be the threshold value for gamma-ray effects (10).

*Analysis for Radioactive Organic Products*

The organic products of the reactions were separated by a programmed temperature gas chromatography column, 2.5 meters long and 5 mm i.d., packed with Dow-Corning silicone grease on a crushed firebrick support. Helium was used as the eluent gas at 50 ml per minute. The irradiated sample was introduced into the column by first freezing it in liquid nitrogen, opening the ampoule, and immediately putting it into a small chamber at the entrance to the column. The column and accessories were arranged so that the sample came in contact with only the glass parts of the equipment. The amount of radioactivity associated with the samples was too low for convenient use of a recorder along with a radioactivity detector which monitored the continuous flow from the chromatographic column (6, 11). A method was therefore developed for concentrating the radiobromine in the effluent in a number of fractions through the use of a series of charcoal tubes put at the outlet of the chromatographic column. The charcoal tubes were cooled by a stream of air through a loose-fitting air condenser. To ensure retention of the low-boiling bromoalkanes with the continued flow of eluent gas, those tubes used to collect extremely volatile substances such as bromomethane were cooled with air which had passed through a coil immersed in liquid nitrogen. In the usual analysis a fraction was collected each minute and the radioactivity was determined by inserting the tube in a well attached to a thallium-activated sodium iodide scintillation crystal.

When the radioactivity of each sample was plotted as a function of time of elution, chromatograms such as in Fig. 1 were obtained. The identity of the activity associated

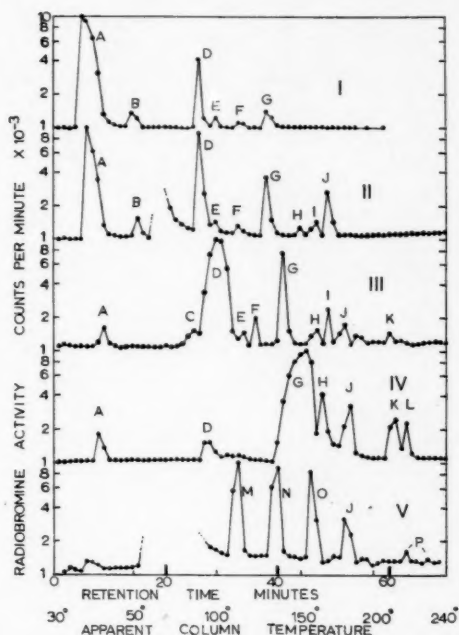


FIG. 1. Examples of chromatograms obtained from neutron-irradiated halomethanes: (I) pure monobromomethane; (II) monobromomethane with about 6 mole% bromine; (III) pure dibromomethane; (IV) pure tribromomethane; (V) tetrachloromethane with about 70 mole% bromine.

The peak assignments are as follows: (A) monobromomethane; (B) monobromoethane; (C) unidentified, probably unsaturated dibromoethane; (D) dibromomethane; (E) 1,1-dibromoethane; (F) 1,2-dibromoethane; (G) tribromomethane; (H) 1,1,1-tribromoethane; (I) 1,1,2-tribromoethane; (J) tetrabromomethane; (K) 1,1,1,2-tetrabromoethane; (L) 1,1,2,2-tetrabromoethane; (M) monobromotrichloromethane; (N) dibromodichloromethane; (O) tribromomono-chloromethane; (P) bromochloroethanes.

In (II) and (V) the discontinuous portion of the curves are for bromine elution.

with the various peaks was inferred in most instances by running macro amounts of known alkyl bromides through the column under the same conditions but using a thermal detector. In other cases, such as for the polybromoethanes, samples were not available and the identities of these have been presumed from boiling-point characteristics and position on the chromatogram (12).

It has been shown (13, 14) that similar results with respect to organic retention and organic products are obtained for both bromine 80 and 82. Therefore in these studies no attempt was made to distinguish between the radioactivity resulting from these two isotopes. In addition, since most of the organic radiobromine activity associated with a sample was determined during an interval of only a few minutes, corrections to a standard time to allow for decay generally amounted to less than 0.2% and were therefore negligible. With an irradiation of normally about 20 hours followed by analysis within a few hours the radioactivity in terms of counts per minute would be divided roughly equally between the two isotopes.

### Analysis for Organic Yield

Organic-yield measurements were made from separate irradiations using the absorption technique previously described (7) with an absorption tube as shown in Fig. 2. The



FIG. 2. Apparatus for organic-yield measurements. (A) Air 15 lb/in<sup>2</sup>. (B) Thermometer capillary allowing about 50 to 100 ml/min air flow. (C) Irradiation vial with sample. (D) Potassium ferrocyanide, 50–100 mesh. (E) Charcoal about 100 mesh, cooled with Dry Ice while air was flowing.

inorganic bromine was retained by the potassium ferrocyanide and the organic compounds were retained by the charcoal. The organic retention was determined by cutting the tube and measuring the radioactivity associated with each part.

### EXPERIMENTAL RESULTS

#### Organic Yield

Although they were not of primary interest, organic-yield measurements were made to enable one to make calculations of the distribution of the total radiobromine among the various organic products. In Fig. 3 are shown the organic-yield results obtained

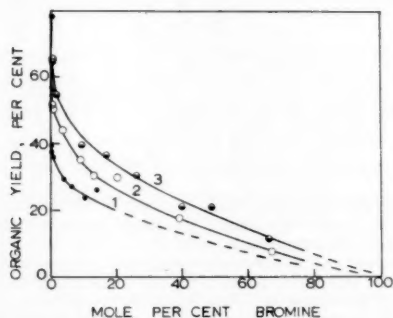


FIG. 3. Organic yield as a function of mole% of bromine: (1) ● monobromomethane; (2) ○ dibromomethane; (3) ● tribromomethane.

with the bromomethanes. These data indicate that the organic yield for pure bromomethanes was much higher than for pure monobromoethane or monobromopropane (8, 15). The organic yield for tribromomethane was comparable to that found previously (16). It is evident from these curves that sensitivity to the scavenging action of small amounts of bromine decreases in the order mono-, di-, and tri-bromomethane.

#### Distribution of Organic Products

Typical chromatograms obtained by the charcoal absorption tube technique for irradiated mono-, di-, and tri-bromomethanes and for a carbon tetrachloride-bromine mixture are shown in Fig. 1. It should be noted that the chromatographic peaks for the parent materials were not so sharp as the other peaks because samples of about 100 to 200 mg of the irradiated bromoalkane were used. This amount of sample caused flooding of the column. In the interests of uniformity, in Fig. 1, the original experimental results were recalculated to a background activity of about 1000 c.p.m. and to a highest peak of 10,000 c.p.m.

Detailed experimental results from irradiated bromomethanes are shown in Tables I and II. A considerable variety of organic products were obtained in each case. The number of products was not so numerous as was found for irradiated bromopropane (6) because, in the former case, the parent molecules contained only one carbon atom. Since the molecular weight of the largest molecules likely to have been formed in the irradiations would be low, the data of Tables I and II include results for all of the probable organic reaction products formed in appreciable amounts.

TABLE I  
Neutron irradiation of monobromomethane - bromine mixtures

Retention time, minutes*	Assignment	Mole% bromine							
		0	0.066	1.96	5.94	11.9	40.8	72.7	84.6
		Percentage of total radiobromine activity							
8	Bromomethane	64.0	34.1	17.8	13.8	11.4	4.5	1.7	0.9
14	Bromoethane	1.7	1.8	0.7	0.5	0.3	0	0	0
27	Dibromomethane	8.6	12.1	8.3	7.7	6.8	4.1	1.9	1.1
29	1,1-Dibromoethane	0.6	0.9	0.6	0.3	0.1	0.05	0.01	0
33	1,2-Dibromoethane	0.5	0.4	0.2	0.3	0.1	0.05	0.01	0
38	Tribromomethane	2.5	3.2	2.9	2.5	2.4	1.7	0.9	0.5
44	1,1,1-Tribromoethane	0	0.2	0.3	0	0	0.01	0	0
46	1,1,2-Tribromoethane	0.3	0.8	0.7	0.3	0.3	0.06	0.01	0
48	Tetrabromomethane	0.2	0.2	1.5	1.4	1.9	1.5	0.9	0.5
57	1,1,1,2-Tetrabromoethane	0	0.1	0.2	0.2	0.3	0.05	0	0
	Inorganic (HBr, Br <sub>2</sub> )†	21.5	46	67	73	76	88	95	97

\*Using programmed temperature chromatography with the temperature program indicated in Fig. 1.

†Estimated from the data of Fig. 3.

TABLE II  
Neutron irradiation of di- or tri-bromomethane - bromine mixtures

Retention time, minutes*	Assignment	Compound irradiated							
		CH <sub>2</sub> Br <sub>2</sub>	CH <sub>3</sub> Br <sub>2</sub>	CH <sub>2</sub> Br <sub>2</sub>	CH <sub>3</sub> Br <sub>2</sub>	CHBr <sub>3</sub>	CHBr <sub>2</sub>	CHBr <sub>3</sub>	CHBr <sub>2</sub>
		Mole% bromine							
		0	2.0	16.0	68.9	0	2.0	18.4	66.1
		Percentage of total radiobromine activity							
8	Bromomethane	1.0	0.9	0.4	0.02	1.0	0.4	0.1	0.01
14	Bromoethane	0.1	0	0	0	0	0	0	0
25	Unidentified	0.5	0	0	0	0	0	0	0
27	Dibromomethane	45.1	28.0	15.8	3.2	1.3	0.8	0.4	0.06
29	1,1-Dibromoethane	0.4	0.2	0.1	0	0.2	0.1	0.03	0
33	1,2-Dibromoethane	1.9	1.4	0.3	0	0.3	0.1	0.03	0.01
38	Tribromomethane	11.6	9.1	6.6	1.9	47.7	31.3	18.1	5.5
44	1,1,1-Tribromoethane	0.8	0	0	0.01	5.1	2.3	0.7	0.01
46	1,1,2-Tribromoethane	1.9	1.7	0.5	0.01	0	0.1	0	0
48	Tetrabromomethane	1.0	3.7	3.9	1.7	4.6	13.6	12.5	5.5
58	1,1,1,2-Tetrabromoethane	0.7	1.5	0.6	0.03	2.9	2.8	1.3	0.09
60	1,1,2,2-Tetrabromoethane	0.4	0.7	0.3	0.02	1.7	1.9	0.8	0.04
70	Pentabromoethane	0	0	0	0	0.06	0.4	0.3	0.01
	Inorganic (HBr, Br <sub>2</sub> )†	34.6	53	72	93	35	46	66	89

\*Using programmed temperature chromatography with the temperature program indicated in Fig. 1.

†Estimated from the data of Fig. 3.

Some experiments involving irradiation of solid tetrabromomethane indicated that radioactive tetrabromomethane was the only organic product formed. Hexabromoethane, whose presence might be expected, was not detectable to the extent of even a trace. In



contrast, carbon tetrachloride when irradiated in the presence of bromine produced bromochloroethanes to a little less than 1% in addition to all the possible bromochloromethanes (Table III). This aspect of the study was not pursued.

TABLE III  
Neutron irradiation of carbon tetrachloride - bromine mixtures

Retention time, minutes*	Radiobromine product assignment	Mole% bromine		
		19	38	70
		Percentage of total radiobromine activity		
33	Monobromotrichloromethane	7.2	5.0	1.7
40	Dibromodichloromethane	5.8	4.8	1.7
46	Tribromomono-chloromethane	2.2	2.3	1.2
52	Tetrabromomethane	0.2	0.2	0.3
63, 67	Haloethanes ( $C_2Cl_3Br_{4-x}$ )	0.6	0.2	0.04
	Inorganic ( $HBr$ , $Br_2$ )†	84	88	95

\*Using programed temperature chromatography with the temperature program indicated in Fig. 1.

†Estimated from data of reference 3.

### DISCUSSION

It is noteworthy that the total yields of the bromoethanes from the mono-, di-, and tri-bromomethanes without bromine were 3.1, 6.2, and 10.3%. These results are reasonable when interpreted in light of the processes leading to the formation of the various products which have been described (4, 5, 8) in terms of a random fragmentation model. In this model the recoiling radiobromine atom and the atoms with which it collides are limited to a "hot spot". When the radiobromine has lost its excess energy it will be in this hot spot of a few hundred cubic Angstroms (17). In this thermalization region, there is a high local concentration of free radicals or ions formed by disruptive collisions during the thermalization of the bromine atom. The bromine atom may combine with one of these fragments during or after thermalization or it may diffuse into the surrounding medium before reaction. The above yields of bromoethanes therefore seem reasonable when it is realized that thermalization would occur in a smaller volume with the tri-bromomethane than with the monobromomethane. There would be a more efficient transfer of energy between the hot radiobromine atom and a highly brominated substrate due to there being a higher "concentration" of atoms of equivalent atomic mass. This more efficient confinement by tribromomethane would give a higher local concentration of the reactive fragments in the thermalization region than would monobromomethane. The higher concentration of reactive fragments would produce the larger proportions of bromoethanes observed since the formation of a bromoethane molecule requires that there be a collision between two one-carbon fragments.

To explain some of the chemical effects of nuclear transformations nine possible elementary reactions involving radiobromine have been discussed (8). On the basis of scavenger effects, the reactions have generally been described as either "hot" or "thermal" by Willard (4, 5). Those reactions involving a thermalized radiobromine atom after it has had an opportunity of undergoing thermal collisions are termed diffusive or thermal and the other reactions are termed hot. If a small amount of bromine scavenger is added to the irradiated substance, the radiobromine will probably exchange with the inactive bromine before it has opportunity to diffuse into the surrounding medium and react to give an organic product. Thus the products of thermal reactions are normally considered

to be those that are readily scavenged. For instance, the percentage of radioactive monobromomethane was decreased from about 64% to 21% in going from 0% to 1 mole% bromine in monobromomethane irradiations. This dramatic decrease must be ascribed almost wholly to the elimination of thermal reactions. The reactions taking place in the radiobromine recoil zone or "hot spot" are relatively insensitive to the presence of scavenger and therefore are generally classed as hot. Hence products formed by these two kinds of reactions are distinguishable by how they are affected by the addition of scavenger.

In Tables I and II are shown data relating to the effect of the addition of bromine scavenger on the amounts of the various products formed. Detailed examination of these data shows that the irradiation products were formed by three classes of reactions instead of the two referred to above. Again, a thermal reaction, i.e. one that was eliminated by a small amount of bromine scavenger, was observed and this type of reaction appeared to be largely confined to the formation of the parent compound. Of the remaining products one group, formed by hot reactions, was insensitive to bromine concentration. In addition, there was a group of products which were gradually suppressed by very high bromine concentration. It is suggested that this last group be termed "hot-spot diffusive".

The hot reactions as considered here may roughly correspond to the "primary recombination" reaction discussed by Noyes (18) in connection with pairs of reactive fragments produced from a molecule. In a similar way, there is possible parallelism between hot-spot diffusive reactions and Noyes' "secondary recombination" reaction. In this connection, it should be pointed out that the hot reactions as discussed here are defined very broadly to include some reactions which are not conventionally thought of as being hot. Thus, the hot reactions of the present system could include, in addition to primary recombination in a "cage", the reactions involving hot replacement of a bromine atom by an energetic radiobromide atom and also reactions involving neutron activation of bromine in an alkyl bromide which fails to rupture the parent carbon-bromine bond. Evidence of the failure of the carbon-bromine bond to rupture in some cases has already been cited (19).

The amount of radioactive parent formed by thermal reactions was estimated from the decrease brought about by the addition of 1 to 2% of bromine to the pure bromomethane. To make a tentative assignment of the amounts of the organic radiobromide products formed by the hot and hot-spot diffusive reactions the data of Table I and II were corrected for the simple dilution effect of increasing amounts of bromine in the bromomethane-bromine mixtures. The formation of an organic radiobromine product in a system containing a hot radiobromine atom in an environment of bromomethane and bromine molecules would depend upon the chance that the atom would encounter a carbon-containing molecule or fragment. Therefore, it was most reasonable to normalize the data by multiplying the observed percentages of the total radiobromine in the various organic molecules by (100/mole% of bromomethane in the mixture). The organic products were divided into groups and, when the normalized data for the groups of products were plotted against the mole per cent of the bromine, in the manner shown in Fig. 4, sets of straight lines were obtained.<sup>3</sup> It can be seen that the results for one group of products were essentially independent of the amount of bromine in the mixture

<sup>3</sup>An alternative set of graphs analogous to those of Fig. 4 were drawn involving atom per cent bromine and involving a normalization on the basis of the number of bromine atoms in the alkyl bromide. The use of those graphs led to virtually the same conclusions as those given in the text. For the reason given, it seemed best to normalize the organic radioactivity in terms of the carbon atoms present in the system.

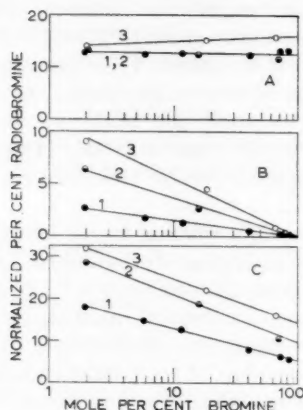


FIG. 4. Normalized organic radiobromine activity as a function of mole% of bromine in bromine-bromomethane mixtures.

(A) Curves for the group of products more highly brominated than the parent: (1) ● di-, tri-, and tetra-bromomethane from monobromomethane as parent; (2) ⊖ tri- and tetra-bromomethane from dibromomethane as parent; (3) ○ tetrabromomethane from tribromomethane as parent.

(B) Curves for the group of products consisting of all others than (A) above or the parent: (1) ● from monobromomethane; (2) ⊖ from dibromomethane; (3) ○ from tribromomethane.

(C) Curves for the parent: (1) ● monobromomethane; (2) ⊖ dibromomethane; (3) ○ tribromomethane.

in the range from 100 to about 1 or 2 mole%. This group consisted of bromomethanes with more bromine than the parent molecule irradiated. Thus, for example, with irradiated dibromomethane this group consisted of tri- and tetra-bromomethane. A second group of products fell on a straight line which extrapolated to zero at the limit of 100 mole% bromine. This group comprised all of the other non-parent organic products. For example, with irradiated dibromomethane these consisted of monobromomethane and all of the bromoethanes. The parent materials formed a third set of straight lines which showed dependence on bromomethane concentration but extrapolated to a finite value at 100 mole% bromine.

The formation of a bromoethane molecule from bromomethane almost certainly must involve a collision of two one-carbon fragments. This implies a diffusive step following the formation of the appropriate one-carbon radicals or ions at the site of thermalization of the radiobromine atom. Since bromine would be an active competitor in reactions involving these fragments, its addition to the system would be expected to decrease the chance of reaction between two one-carbon fragments. Hence, the bromoethanes should be formed nearly exclusively in the hot-spot or thermalization zone. In order for the reaction to be significantly scavenged the concentration of scavenger would have to be comparable to the concentration of the reacting fragments in the reaction zone. The mole per cent of reactive fragments in the hot spot would be expected to be high and hence the bromine concentration must also be high to bring about a significant decrease in the extent of reaction leading to the formation of bromoethanes. It can be seen from Fig. 4B and Tables I and II that, although at 50 mole% bromine the fraction of these products was notably reduced, they could be considered to be completely scavenged only when the mole per cent of bromine approaches 100. Thus, these are hot-spot diffusive products. The chance of two fragments from bromomethane molecules colliding outside of the hot spot would be remote and hence the formation of bromoethanes by thermal

reactions does not occur to an appreciable extent. The observation that traces of bromine had little effect on the proportions of those products bears out the contention that they were not formed outside the thermalization region. In this connection, it is noteworthy that the formation of bromoethanes from monobromomethane was even enhanced by a trace of bromine since 4.2% of bromoethanes was obtained with 0.066 mole% bromine while 3.1% was obtained when no bromine was present. This increase may have been due to an efficient scavenging of the hydrogen atoms or ions formed during thermalization. If hydrogen atoms or ions were scavenged more readily than the other fragments, there could be an increased formation of products resulting from recombinations of the remaining fragments, providing, of course, that the bromine concentrations were not too high. The hot-spot diffusive products discussed above appear to include the bromomethanes with less bromine than the parent molecule. Such products must be formed from an extensively fragmented bromomethane and radiobromine. For instance, to obtain radioactive monobromomethane from irradiated tribromomethane at least two and probably three carbon-bromine bonds must have been broken. It is not unreasonable to suppose that the one-carbon fragment and the radiobromine would have to diffuse together to form the product.

The products which persisted (Fig. 4A) in spite of large amounts of bromine must have been formed by hot processes (8) involving direct reaction of the recoiling radiobromine and a molecule or fragment in its environment. The extent of formation of products from this type of reaction should be independent of the concentration of the bromine scavenger after allowance is made for the dilution effect of the increasing amounts of bromine. It appears from these data that the hot products include all the bromomethanes with more bromine than the parent.

The lines in Fig. 4C suggest that in the presence of bromine the parent was formed by both hot and hot-spot diffusive reactions. It is proposed that the values obtained by extrapolation to 100 mole% of bromine are measures of the parent radiobromine-containing molecules formed by hot reactions. Similarly, radioactive parent formed in excess of this extrapolated value in the presence of a trace of bromine are measures of that formed by hot-spot diffusive recombination of radiobromine with an appropriate radical, ion, or molecule. As pointed out earlier, an estimate of the parent formed by thermal reactions was obtained from the effect of a small amount of bromine. It would thus appear that radioactive parent was formed by all three modes of reaction.

In Table IV are shown estimates made on the basis of the preceding discussion of the

TABLE IV  
Estimated amounts of products formed by hot, thermal, and  
hot-spot diffusive reactions

Material irradiated	Percentage of total radiobromine activity				
	Parent			Non-parent organic	
	Hot	Hot-spot diffusive	Thermal	Hot	Hot-spot diffusive
CH <sub>3</sub> Br	5.4	16	41	13*	2.5†
CH <sub>2</sub> Br <sub>2</sub>	9.4	21	15	13‡	6§
CHBr <sub>3</sub>	14.3	20	5 to 10	14	9¶

\*Di-, tri-, and tetra-bromomethanes.

†All bromoethanes.

‡Tri- and tetra-bromomethanes.

§Monobromomethane and bromoethanes.

¶Tetrabromomethane.

||Mono- and di-bromomethane and bromoethanes.

distribution, according to the three types of reactions, of the products which made up the 78%, 65%, and 65% organic yield observed for mono-, di-, and tri-bromomethane (Tables I and II). It is interesting that the amount of parent formed by hot reactions was approximately in the ratio of 1 to 2 to 3 for mono-, di-, and tri-bromomethane. It would suggest that the chance of forming radioactive parent molecules by the types of hot reactions previously mentioned was directly proportional to the number of bromine atoms in the molecule.

#### ACKNOWLEDGMENTS

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## PERFLUOROALKYL DERIVATIVES OF TIN

### II. DIMETHYLTRIFLUOROMETHYLTIN CHLORIDE<sup>1,2</sup>

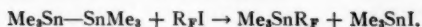
R. D. CHAMBERS, H. C. CLARK, AND C. J. WILLIS

#### ABSTRACT

A methyl group is cleaved by chlorine in preference to trifluoromethyl from trimethyltrifluoromethyltin and dimethyltrifluoromethyltin chloride; the significance of this is discussed in terms of the electronegativity of the trifluoromethyl group. The influence of trifluoromethyl on the acceptor properties of the tin atom in dimethyltrifluoromethyltin chloride has been illustrated by means of conductivity measurements. Nuclear magnetic resonance measurements of trimethyltrifluoromethyltin and dimethyltrifluoromethyltin chloride are also reported.

#### INTRODUCTION

Perfluoroalkyl derivatives of tin have been prepared recently by the reaction of hexamethylditin with perfluoroiodoalkanes (1, 2, 3),



The reaction has since been shown to be applicable to other compounds containing metal-metal, or metalloid-metalloid, bonds and has led to the synthesis of new perfluoroalkyl compounds of arsenic (4) and phosphorus (5). Tin is the most electropositive element for which a stable trifluoromethyl derivative has been prepared, and the resultant compound has been shown to have interesting properties (1, 11). Because of this, and also because of the valuable synthetic properties of alkyltin halides, we have studied further the halogenation of trimethyltrifluoromethyltin.

#### EXPERIMENTAL

##### *Preparation of Trimethyltrifluoromethyltin*

Trimethyltrifluoromethyltin was prepared by irradiating, with ultraviolet light, a mixture of hexamethylditin and excess trifluoroiodomethane contained in a Carius tube. The details of this preparation have been described (1, 3).

##### *Chlorination of Trimethyltrifluoromethyltin*

Chlorine (2.68 g, 38 mmoles) was condensed into a Carius tube which contained a solution of trimethyltrifluoromethyltin (9.5 g, 41 mmoles) in chloroform (15 ml). The tube was sealed under vacuum and transferred to a cooling bath at  $-46^\circ$ ; the bath was allowed to warm to room temperature and after 2 days the reaction mixture had become colorless. Volatile material was removed under vacuum and, apart from chloroform, it consisted essentially of methyl chloride, together with small amounts of chlorotrifluoromethane and fluoroform. A white solid remained from which dimethyltrifluoromethyltin chloride (8 g, 77% yield), m.p.  $46-47^\circ$ , was sublimed *in vacuo* at  $60-70^\circ$ .

##### *Chlorination of Dimethyltrifluoromethyltin Chloride*

Chlorine (0.75 g, 10.6 mmoles) was condensed into a Carius tube which contained a solution of dimethyltrifluoromethyltin chloride (2.55 g, 10.1 mmoles) in carbon tetrachloride (15 ml). The color due to the chlorine did not appear to have diminished after 10 days and therefore the tube was warmed to  $60^\circ$  for 48 hours, during which time the

<sup>1</sup>Manuscript received September 2, 1960.

Contribution from the Chemistry Department, University of British Columbia, Vancouver 8, B.C.

<sup>2</sup>Part I. H. C. Clark and C. J. Willis. *J. Am. Chem. Soc.* **82**, 1888 (1960).

mixture had become colorless. The volatile material was distilled into a vacuum system and then fractionated. A fraction condensing at  $-195^{\circ}$  (0.10 g) was shown by infrared examination to consist of chlorotrifluoromethane together with a small amount of fluoroform; the fraction condensing at  $-132^{\circ}$  (0.44 g) consisted mainly of methyl chloride and a small amount of some unidentified material. A white solid (1 g) remained in the Carius tube; the solid was triturated with carbon tetrachloride and the mixture filtered. The filtrate was evaporated, leaving a solid (0.6 g) which melted at  $103^{\circ}$ . Dimethyltin dichloride melts at  $106^{\circ}$ ; a mixed melting point gave no depression. The insoluble residue did not melt below  $200^{\circ}$ ; it contained no chlorine and analyzed: C, 9.51; H, 1.57; F, 37.54. The infrared spectrum (Nujol mull) showed strong bands at 1150 and  $1080\text{ cm}^{-1}$ , which are characteristic of C—F stretching modes for trifluoromethyl attached to tin (trimethyltrifluoromethyltin and dimethyltrifluoromethyltin chloride give almost identical absorption in this region (1)). A band at 800 (m) was present, which is characteristic of a tin-methyl rocking mode (1). Thus, from the analysis and infrared spectrum, the residue appears to contain methyl, trifluoromethyl, and fluoride in the ratio 1:1:2.

#### *Conductometric Measurements*

Measurements were carried out using a standard a-c. bridge. The cell used was fitted with a stopper to prevent evaporation of the solutions; and the cell constant was found to be 0.2958 by using a standard aqueous solution of potassium chloride, made up by weight.

#### *Titration of Dimethyltrifluoromethyltin Chloride in Nitrobenzene with Pyridine*

Nitrobenzene was purified by several distillations, and "Analar" grade pyridine was used. Additions of liquid to the cell were made by means of a weight pipette which incorporated a "Teflon" stopcock.

A solution of dimethyltrifluoromethyltin chloride (0.344 g) in nitrobenzene (60 g) was added to the cell. For the initial measurements a solution of pyridine (8 g) in nitrobenzene (50 g) was added from the weight pipette. Pure pyridine was used for the later measurements.

The titration of trimethyltin chloride (0.27 g) in nitrobenzene (59.63 g) was carried out in the same manner.

#### *Dissociation Constant of Dimethyltrifluoromethyltin Chloride in Absolute Ethanol*

Kraus and Callis (6) found that trimethyltin chloride behaved as a weak electrolyte in ethanol and that a dissociation constant could be determined. We have carried out the same procedure for dimethyltrifluoromethyltin chloride. The specific conductance of a solution of dimethyltrifluoromethyltin chloride in absolute ethanol was measured at various concentrations up to  $1.50 \times 10^{-2}$  moles per liter, and a graph was drawn of specific conductance as abscissa against the reciprocal of equivalent conductance as ordinate. If the "law of mass-action" can be applied, then the slope of the graph represents  $(1/K_{\text{dis}}\Lambda_0^2)$  and the intercept with the ordinate represents  $(1/\Lambda_0)$ . The graph was a straight line up to a concentration of  $0.59 \times 10^{-2}$  mole per liter (showing that the "law of mass-action" can be applied in this case) with a slope  $2.016 \times 10^5$  and intercept with the ordinate 0.14, giving  $K_{\text{dis}} = 9.73 \times 10^{-5}$  moles per liter at  $25^{\circ}$  (Table II).

#### *Proton and Fluorine Resonance Spectra*

The measurements were made at a fixed frequency of 40 Mc/sec on a Varian Model V-4300B high-resolution N.M.R. spectrometer. An internal standard (benzene) was used for the proton resonance, using carbon tetrachloride as solvent, and an external standard

TABLE I

Proton resonance spectra*			Fluorine resonance spectra†	
Compound	Shift	Increment	Compound	Shift
Me <sub>4</sub> Sn	286	—	Me <sub>3</sub> SnCF <sub>3</sub>	1165
Me <sub>3</sub> SnCl	266	20	Me <sub>2</sub> CF <sub>3</sub> SnCl	1128
Me <sub>3</sub> SnBr	264	22		
Me <sub>3</sub> SnCl <sub>2</sub>	251	35		
Me <sub>2</sub> SnCF <sub>3</sub>	279	7		
Me <sub>2</sub> CF <sub>3</sub> SnCl	264	22		

\*Chemical shift (in cycles per second) from the resonance of benzene (internal standard).

†Chemical shift (in cycles per second) from the resonance of trifluoroacetic acid (external standard).

TABLE II

Dimethyltrifluoromethyltin chloride in absolute ethanol at 25°

Conc. $\times 10^4$ , equiv. per liter	Specific conductance, $\text{l.} \times 10^7$	Equivalent conductance
0.3615	2.16	5.98
0.9757	4.47	4.58
1.712	6.19	3.62
3.672	10.53	2.87
4.647	12.03	2.70
18.12	26.60	1.47
19.92	28.13	1.41
37.76	40.00	1.06
59.69	51.30	0.859
79.29	66.58	0.840
13.01	80.00	0.615
150.7	88.94	0.590

(trifluoroacetic acid) was used for the fluorine resonance. The sample concentration used was 10–15%, and 2–5% benzene. A "side-banding" technique was used for these determinations.

## DISCUSSION

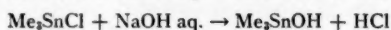
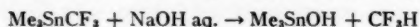
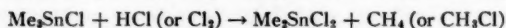
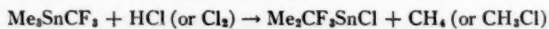
The reaction of trimethyltrifluoromethyltin with an equimolar quantity of chlorine has previously been studied (1); a methyl group was easily removed at room temperature giving methyl chloride and dimethyltrifluoromethyltin chloride. This reaction has now been carried out in chloroform solution and improved yields have been obtained. Further chlorination of dimethyltrifluoromethyltin chloride in carbon tetrachloride, with an equimolar quantity of chlorine, was considerably more difficult and required heating to 60° for 2 days to complete the reaction. A complex mixture of volatile products was obtained which could not be completely separated by fractionation and was investigated spectroscopically. The two isolated fractions were methyl chloride, containing a small amount of some unidentified material, and trifluorochloromethane. Traces of fluoroform were also detected. The ratio of the weights of these two fractions, taken in conjunction with their infrared spectra, showed that the ratio of methyl chloride to trifluorochloromethane in the products was approximately 8:1.

The solid residue was separated by extraction with carbon tetrachloride into dimethyltin dichloride and a white intractable solid which was shown by analysis and its infrared spectrum to contain methyl, trifluoromethyl, and fluoride in the ratio, 1:1:2. It is clear,

then, that preferential removal of a methyl group occurred, followed by rearrangement of the products. The formation of fluorides most likely takes place through the elimination of difluorocarbene from trifluoromethyl. The difluorocarbene eliminated might interact with some of the compounds present and greatly increase the complexity of the reaction mixture. Decomposition of trimethyltrifluoromethyltin and dimethyltrifluoromethyltin chloride has already been shown to occur in this way. A similar reaction of dimethyltrifluoromethyltin chloride with two equivalents of chlorine gave an equally complex mixture and no trifluoromethyltin trichloride could be isolated. The failure to isolate this compound may be due to its low thermal stability, which would be in accord with the much lower stability of dimethyltrifluoromethyltin chloride as compared with trimethyltrifluoromethyltin.

Thus, the tendency for a methyl group to be eliminated in preference to trifluoromethyl, at least in the first two stages of chlorination, has been illustrated. It has been shown by other workers (8) that the cleavage of organotin compounds by electrophilic reagents follows the empirical rule that the most electronegative group is preferentially eliminated and, on this basis, the cleavage of methyl in preference to trifluoromethyl is surprising. It has been shown (8) that the perfluorovinyl group is very easily cleaved by electrophilic reagents, and that it falls into the cleavage series of  $\text{CF}_2=\text{CF}$ ,  $\text{C}_6\text{H}_5 > \text{CH}_3 > \text{CF}_3$ . It has been postulated (9) that such cleavage series may be explained in terms of electrophilic attack on the carbon atom with the highest electron density, and other workers (10) have suggested that, because of the inductive effect of the fluorine atoms, the carbon atom of the trifluoromethyl group is more electron deficient than the carbon atoms of the methyl groups in trimethyltrifluoromethyltin. This view does not take into account the ability of the trifluoromethyl group to behave as a separate electronegative entity, as illustrated by the removal of a trifluoromethyl group from trimethyltrifluoromethyltin by boron trifluoride (11). These compounds react under anhydrous conditions, in an inert solvent, with transfer of a trifluoromethyl anion to the boron trifluoride forming the very stable  $[\text{BF}_3\text{CF}_3]^-$  ion. There is clearly a considerable difference in the behavior of the two electrophilic reagents, chlorine and boron trifluoride.

Lagowski (12) has concluded on the basis of thermochemical and infrared data that the value of the effective electronegativity of the trifluoromethyl group lies between those of fluorine and chlorine. Although other factors must also be involved, it is interesting then to note the similar behavior of the trifluoromethyl group and halogens in organotin compounds, with respect to cleavage reactions.



It appears that as a result of its high electronegativity the trifluoromethyl group in trimethyltrifluoromethyltin is attached to the tin atom by a highly polarized bond, and, as such, differs from other organic groups which have been attached to a tin atom and placed in the cleavage series. The importance of this polarity in determining the properties of certain organotin compounds has recently been considered by Seyferth and Kahlen (13), who have discussed the properties of trimethyltin cyanide in terms of the highly polarized tin-carbon bond of the cyanide group.

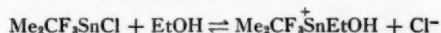
In the cleavage of trimethyltrifluoromethyltin by electrophilic reagents, the relative

tin-carbon bond energies resulting from the polarized nature of the tin-trifluoromethyl bond may then be the controlling factors. Cleavage of a methyl in preference to a trifluoromethyl group on reaction with chlorine under non-polar conditions may result from the presence of this highly polarized bond which, by its influence on the tin-carbon bond energies, may make this elimination energetically favorable.

Trimethyltin chloride will react with pyridine and ammonia to form stable 1:1 co-ordination compounds, whereas dimethyltin dichloride adds on two donor molecules (14). It was our aim to prepare similar complex compounds using dimethyltrifluoromethyltin chloride, establish their constitution, and hence compare trifluoromethyl and chlorine with respect to their influence on the acceptor properties of an adjoining tin atom. We were not able to isolate complex salts, since direct reaction with pyridine gave a solid which did not contain trifluoromethyl. It was therefore necessary to use conductometric measurements in order to illustrate the acceptor properties of the tin atom in dimethyltrifluoromethyltin chloride.

It has been shown (15) that trimethyltin chloride is non-conducting in non-donor solvents and that addition of pyridine to a solution of trimethyltin chloride in nitrobenzene is accompanied by a rise in conductivity of the solution. Trimethyltrifluoromethyltin was found to be non-conducting in nitrobenzene and no significant rise in conductivity was observed with the addition of pyridine, indicating that there was little or no tendency to form a co-ordination compound which could yield ionic species. We have also compared the changes in conductivity of equimolar solutions of trimethyltin chloride and dimethyltrifluoromethyltin chloride in nitrobenzene ( $2.7 \times 10^2$  moles of chloride per liter) with the addition of pyridine. Dimethyltrifluoromethyltin chloride was non-conducting in nitrobenzene but the conductivity rose very sharply with the addition of pyridine (Fig. 1) in an analogous manner to trimethyltin chloride (Fig. 2). The specific conductance of a  $0.015 M$  solution of dimethyltrifluoromethyltin chloride in ethanol, which is a solvent of lower dielectric constant than nitrobenzene, was found to be  $88.94 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Thus, conducting species are formed, presumably due to co-ordination of pyridine to the tin atom in dimethyltrifluoromethyltin chloride. The resulting co-ordination complex appears to be a much stronger electrolyte than the corresponding complex between trimethyltin chloride and pyridine, since the conductivity of the dimethyltrifluoromethyltin chloride solution rises much more quickly than that of trimethyltin chloride (compare Fig. 1 and Fig. 2) for equivalent amounts of pyridine added during the first part of the experiment. The maximum values of specific conductance reached were  $7.54 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  for dimethyltrifluoromethyltin chloride, and  $11.25 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  for trimethyltin chloride.

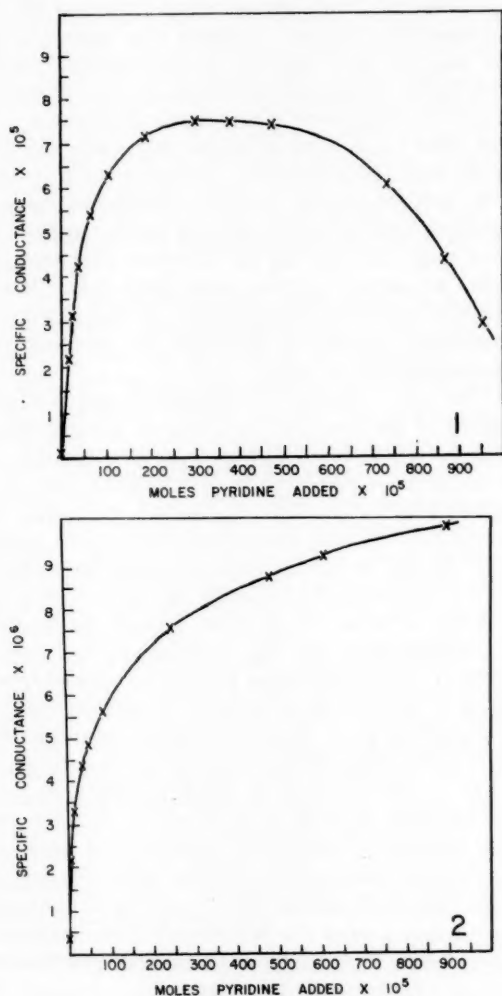
A dissociation constant for the reaction



was determined by the method used by Kraus and Callis (6) and found to be  $9.7 \times 10^{-8}$  moles per liter at  $25^\circ \text{C}$  (cf.  $3.5 \times 10^{-8}$  moles per liter at  $25^\circ \text{C}$  for trimethyltin chloride). The strong inductive effect of the trifluoromethyl group probably increases the acceptor properties of the tin atom, thus increasing the ionization of any co-ordination complex.

During the titration of dimethyltrifluoromethyltin chloride, after a concentration of  $7.42 \times 10^{-2}$  moles of pyridine per liter had been reached (Fig. 1) a further reaction occurred. The conductivity of the solution decreased and this was accompanied by the appearance of a precipitate in the cell; analysis and the infrared spectrum showed that this compound did not contain trifluoromethyl, and that it was identical with the uncharacterized





FIGS. 1 and 2.

compound obtained by direct reaction of pyridine and dimethyltrifluoromethyltin chloride. The nature of this secondary reaction was not investigated further.

We have attempted to extend the anionic transfer reaction with boron trifluoride, by adding trimethyltrifluoromethyltin to other acceptor molecules where the formation of complex ions is possible.

Preliminary experiments (16) have shown that compounds of the type  $\text{Me}_3\text{Sn}[\text{MCl}_3\text{X}]$  (where  $\text{M} = \text{Al}$  or  $\text{Ga}$ , and  $\text{X} = \text{halogen}$ ) can be prepared. However, reaction between aluminum trichloride or gallium trichloride and trimethyltrifluoromethyltin did not yield complex compounds of the form  $\text{Me}_3\text{Sn}[\text{MCl}_3\text{CF}_3]$ , ( $\text{M} = \text{Al}$  or  $\text{Ga}$ ). Further

investigation of complex compounds involving trimethyltin and dimethyltin cations is proceeding.

Thus the reactions of trimethyltrifluoromethyltin with chlorine and with boron trifluoride demonstrate the "halogen-like" character of the trifluoromethyl group. The foregoing results show, however, that this analogy has several limitations, particularly under conditions where reaction with the trifluoromethyl groups leads to its decomposition.

Brown and Webster (17) have determined the changes in chemical shift in the proton resonance of a series of methyltin chlorides  $[\text{Me}_x\text{SnCl}_{4-x}]$  and have observed approximately equal increments for each methyl group replaced by chlorine, from tetramethyltin to methyltin trichloride. We have also observed this effect and have determined the proton and fluorine chemical shifts in trimethyltrifluoromethyltin and dimethyltrifluoromethyltin chloride. These results are shown in Table I and, since all shifts are to low field, an increase of shift corresponds to a decrease in the shielding. The increment of shift from tetramethyltin caused by the introduction of trifluoromethyl is not of the same order as the increment due to introduction of a halogen atom. This, however, cannot be taken as a comparison of the chemical similarity of trifluoromethyl and halogens since chemical shift appears to depend on so many factors other than electronegativity (18).

#### ACKNOWLEDGMENTS

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## COCATALYSIS IN FRIEDEL-CRAFTS REACTIONS

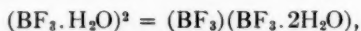
### IV. BORON FLUORIDE - METHANOL<sup>1</sup>

JOAN M. CLAYTON<sup>2</sup> AND A. M. EASTHAM

#### ABSTRACT

The kinetics of the isomerization of *cis*- and *trans*-2-butenes, catalyzed by methanol and boron fluoride mixtures, have been studied. The rate was found to be proportional to the concentrations of the boron fluoride - methanol complex and of free boron fluoride but independent of the butene concentration.

In previous papers (1, 2) we have reported the results of some experiments on the isomerization of *cis*- and *trans*-2-butenes in ethylene dichloride solution, using boron fluoride - water mixtures as catalyst. In order to interpret the results of those experiments it was necessary to estimate the position of the equilibrium between the mono- and di-hydrates of boron fluoride,



and this was done from measurements of the vapor pressure of boron fluoride over solutions of water in ethylene dichloride. From the resulting values for the concentrations of the hydrates it was concluded that the rate expression for the conversion of one butene isomer into the other was

$$d(\text{isomer}_B)/dt = k(\text{BF}_3)(\text{BF}_3 \cdot \text{H}_2\text{O})(\text{isomer}_A).$$

The equilibrium constant obtained for the monohydrate-dihydrate reaction was at best an approximate one for, as its measurement was dependent upon small differences between large numbers, a considerable error was possible. With the catalyst system boron fluoride - methanol, however, this uncertainty can be largely avoided because the dialcoholate is very much less stable than the monoalcoholate and one may therefore assume that the concentration of the latter is approximately that of the added alcohol. Furthermore, the rates are much slower, and hence more easily measured, than those with water as cocatalyst, the catalyst mixtures are completely soluble over a wide range of concentrations, and the higher vapor pressure of the methanol permits more accurate dispensing of the cocatalyst. The present paper reports the results of some studies of the isomerization of the 2-butenes by boron fluoride - methanol mixtures.

#### EXPERIMENTAL

Materials were prepared and handled essentially as previously described. Methanol was dried with magnesium methoxide and measured as the vapor at pressures well below the saturation vapor pressure at room temperature.

Rates were measured in a reaction flask equipped with a manometer and having a total free space of about 215 ml. Ethylene dichloride (35 ml) was used as solvent and the temperature was controlled at 20° C by water circulating around the flask. Samples were removed as previously described and analyzed either by infrared spectroscopy or by gas chromatography. Isomerization of the *trans* isomer was followed by the appearance

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of the *cis* peak in the infrared spectrum while that of the *cis* isomer was followed by the appearance of the *trans* peak in the chromatogram of a column prepared from 30 g silver nitrate dissolved in 30 ml glycerine, supported on 58 g Celite and packed into 16 feet of stainless steel tubing. The chromatographic method is suitable for mixtures containing up to about 75% of the *trans* isomer and is more accurate than the spectrographic method because it is not affected by traces of solvent. At low *cis* concentrations, however, the peaks for the two isomers overlap in the chromatogram and the infrared method gives the better results if a correction is made for the small absorption due to residual solvent.

The vapor pressure of boron fluoride over solutions of methanol in ethylene dichloride is shown in Fig. 1 and indicates clearly the essentially quantitative formation of the

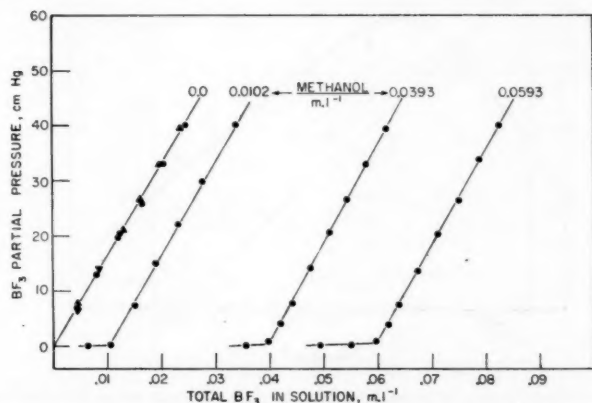


FIG. 1. The vapor pressure of boron fluoride over solutions of methanol in ethylene dichloride.

1:1 complex at all boron fluoride concentrations in excess of the methanol (compare the corresponding data for water (2)).

In this paper most concentrations have been expressed as moles per liter, calculated from the number of moles of reactant introduced into the reaction vessel divided by the volume of solvent. Concentrations expressed in this way give a reasonably accurate statement of the amount of dissolved material when the vapor pressure of the reactant is low, e.g. the methanol - boron fluoride complex, and are also quite accurate for the butenes since about 95% of the added olefin is in solution under the conditions of these experiments. In the case of boron fluoride, however, since about 80% of the free reagent is in the gas phase, the following terms, all based on the volume of solvent, have been used to define the concentrations:

$(BF_3)_{total}$  = the total  $BF_3$  added to the system whether complexed, dissolved, or in the gas phase.

$(BF_3)_{free}$  = all uncomplexed  $BF_3$  whether dissolved or in the gas phase.

$(BF_3)_{solution}$  = that part of the free  $BF_3$  (about 20%) which is in solution.

## RESULTS

In Fig. 2, the initial rates of isomerization of *trans*-2-butene are shown for a series of experiments in which the methanol concentration was varied at constant concentrations

of butene and of total boron fluoride (1.0 mole  $\text{l}^{-1}$  and  $6.0 \times 10^{-3}$  moles  $\text{l}^{-1}$  respectively). It is evident that the variation in rate is essentially similar in type to that observed for cocatalysis by water (1), but the rates are much slower. Because of differences in temperature, in the free space of the reaction vessel, and perhaps in the kinetics, the relative rates for the two cocatalysts cannot be estimated accurately but for the conditions of this particular set of experiments, water appears to be about 50 times as effective as methanol.

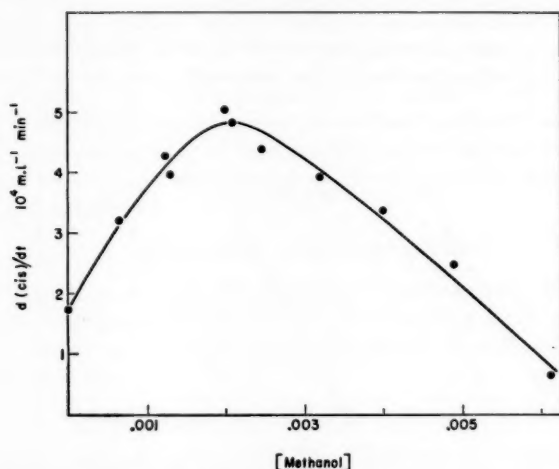


FIG. 2. The rate of isomerization of *trans*-2-butene at constant total boron fluoride concentration and varying methanol concentration.

The kinetics were examined in more detail by varying each of the three reactants in turn. For the experiments shown in Fig. 3(a) the initial *trans*-butene and methanol concentrations were fixed at 1.0 mole  $\text{l}^{-1}$  and  $2.1 \times 10^{-3}$  moles  $\text{l}^{-1}$ , respectively, and the boron fluoride concentration was varied. For the experiments of Fig. 3(b) the *trans*-butene concentration was again 1.0 mole  $\text{l}^{-1}$  but the methanol concentration was varied and the boron fluoride adjusted to produce a constant  $1.0 \times 10^{-2}$  moles  $\text{l}^{-1}$  excess over the methanol. The dependence of the rate upon the concentrations of both free boron fluoride and the methanol - boron fluoride complex appears to be of the first order.

The dependence of the rate upon butene concentration is rather more difficult to determine, especially in the conversion of the *trans* to the *cis* isomer. In the previous work with water as cocatalyst, the limited evidence available suggested a first-order dependence on butene but the present results show clearly an order approaching zero (Table I). Furthermore the initial rates are almost identical when either isomer is used as starting material, indicating that the equilibrium is not determined primarily in the rate-controlling step. There is some indication in the experiments with *trans*-butene that the rates may not be entirely independent of the butene concentration but as the divergence is greatest where the experimental error is greatest we are inclined to believe that the data for the *cis* isomer are the more reliable.

The rate constants in the above table must be regarded as peculiar to the present



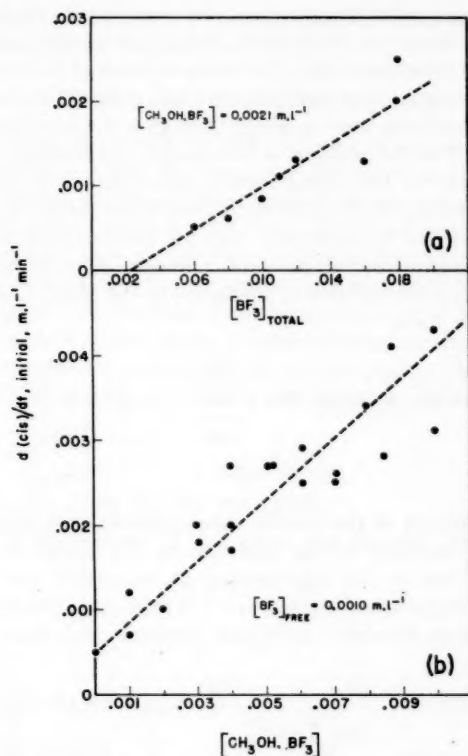


FIG. 3. The rate of isomerization of *trans*-2-butene: (a) at constant concentration of  $\text{CH}_3\text{OH} \cdot \text{BF}_3$ ; (b) at constant concentration of free boron fluoride.

TABLE I

Initial butene, moles l. <sup>-1</sup>	$k_{\text{obs}}$	$k_{\text{initial}}$	Initial butene, moles l. <sup>-1</sup>	$k_{\text{obs}}$	$k_{\text{initial}}$
cis, 2.0	.0030	.0026	trans, 2.75	.0033	.0027
1.0	.0020	.0020	2.0	.0032	.0024
0.50	.0023	.0023	1.5	.0028	.0025
0.25	.0021	.0022	1.0	.0017	.0018
0.125	.0021	.0019	0.5	(.0010)	(.0010)
Average .0023 moles l. <sup>-1</sup> min <sup>-1</sup>			Average .0024 moles l. <sup>-1</sup> min <sup>-1</sup>		

apparatus where about 80% of the free boron fluoride is in the gas phase. For purposes of comparison with other work, the value of  $k'$  in the expression

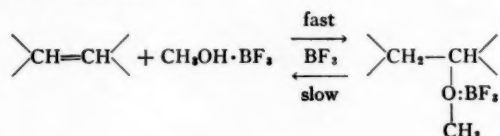
$$dx/dt = k'(\text{CH}_3\text{OH} \cdot \text{BF}_3)(\text{BF}_3)_{\text{solution}}$$

may be assigned the value  $4.0 \times 10^2 \text{ l. mole}^{-1} \text{ min}^{-1}$ .

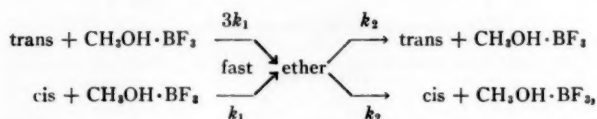
Polymerization of the butene becomes important at high reactant concentrations and can be observed by the falling vapor pressure of the solutions. A few data gathered

throughout the course of this work suggest that the rate of polymerization is strongly dependent upon the concentrations of butene and of the methanol-boron fluoride complex but seemingly less dependent upon the concentration of free boron fluoride. The present evidence does not suggest that isomerization and polymerization are the parallel reactions one would expect if both were to occur through a common intermediate (e.g. a carbonium ion). This aspect of the problem is now under investigation.

The zero-order dependence of the isomerization upon butene concentration suggests either that butene reacts rapidly with catalyst to form a relatively stable intermediate, or else that the rate is controlled by some slow step not involving butene as for example a reaction between the two catalyst components. The only obvious stable intermediate would be the ether resulting from addition of methanol to the olefin (2-methoxy-butane), and indeed a reaction of the form



could account completely for all of the kinetic data reported here. If one assumes that equilibrium is determined entirely in the addition of the boron fluoride-methanol complex to the olefin and not in the regeneration of the olefin, that the equilibrium mixture contains only the cis and trans isomers in a 1:3 ratio, that steady-state conditions apply to the unreacted boron fluoride-methanol complex, and that all reactions are



catalyzed by free boron fluoride, then the following integrated rate expressions are obtained for the reactions:

$$\begin{aligned} \text{trans} \rightarrow \text{cis} \quad k_{\text{obs}} t &= \frac{3a}{8} \ln \frac{a}{a-4x} - \frac{x}{2}, \\ \text{cis} \rightarrow \text{trans} \quad k_{\text{obs}} t &= \frac{3a}{8} \ln \frac{3a}{3a-4x} + \frac{x}{2}. \end{aligned}$$

In these expressions  $a$  is the initial concentration of one isomer,  $x$  the concentration of the other formed in time  $t$ , and  $k_{\text{obs}} = k_2 (\text{CH}_3\text{OH} \cdot \text{BF}_3)_{\text{initial}} / (\text{BF}_3)_{\text{free}}$ . The values of  $k_{\text{obs}}$  obtained from these expressions hold very well over one or two half-lives of the reactions and agree reasonably well with the values obtained from initial rates (Table I).

However, although a treatment of this kind seems to account for these data, more recent experiments in this laboratory indicate that the isomerization cannot occur in this way. The addition and elimination of methanol do indeed occur under boron fluoride catalysis, but the rates seem to be too slow to explain the isomerization. It is possible that some other intermediate less stable than the ether is involved but it is difficult to conceive of one which would not be in equilibrium with free butene.

If the reaction does not involve a stable intermediate then presumably some reaction of the catalyst system, as, for example,



must be rate controlling. A reaction of this kind would explain the need for free boron fluoride in the isomerization but we have been reluctant to postulate intermediates in which two boron fluoride molecules are attached to one oxygen atom because of the absence of any independent evidence for them. Their existence as transitory species is not, however, impossible. One of the difficulties with this approach is that it suggests the direct protonation of olefins to form carbonium ions and there is a growing body of evidence which suggests that, because of the high reactivity of such ions, their formation is not readily reversible (3) and hence cannot account for the rapid isomerization. A loosely bound proton-olefin complex such as a  $\pi$ -complex would, on the other hand, be reversible but probably would not disturb the olefin structure sufficiently to produce isomerization.

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# CONTRIBUTION À L'ÉTUDE DE LA RÉACTION DE VON RICHTER

## I. SUR L'IDENTIFICATION DE QUELQUES PRODUITS ACIDES<sup>1</sup>

E. CULLEN<sup>2</sup> ET PH. L'ÉCUYER

### RÉSUMÉ

La réaction de von Richter avec le *p*-chloronitrobenzène fournit, outre l'acide *m*-chlorobenzoïque attendu, un mélange de produits dont le 4,4'-dichloro-2,2'-dicarbamylazobenzène, le 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol et l'acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique. Ce dernier se transforme en la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazol-(2)]-benzoïque par sublimation.

Avec le nitrobenzène, outre l'acide benzoïque, seul le 6-cétoquinazolo[1,2,2',3']indazol a été isolé.

Dans le but de déterminer la position des substituants dans les dérivés du nitrobenzène, von Richter (1, 2, 3) a fait réagir les dérivés nitrés du nitrobenzène avec le cyanure de potassium en solution alcoolique. Comme il obtenait des acides carboxyliques et que la réaction était invariablement accompagnée de la perte d'un groupe nitré, il supposa que le groupement nitrile substituait le groupe nitré et se transformait en groupement carboxylique. Toutefois, à la suite d'études de structures exécutées concurremment par Griess (4) et Korner (5), von Richter (6) dut admettre que le groupement nitrile se fixe en ortho de la fonction éliminée au lieu de déplacer directement le groupe nitré, ce qui a depuis été vérifié par Holleman (7) et tout récemment par Bunnett, Cormack et McKay (8). La transformation du *p*-bromonitrobenzène en acide *m*-bromobenzoïque peut servir d'exemple de cette réaction.

Sauf le travail de Holleman, la réaction est demeurée dans l'oubli jusqu'en 1950 alors que Bunnett et des collaborateurs (8, 9, 10) entreprirent d'en étudier la portée et le mécanisme. En plus de confirmer les résultats déjà obtenus par von Richter, ces chercheurs ont étendu le champ des observations antérieures. Ils ont, en particulier, montré qu'il est préférable de faire bouillir les réactifs dans l'alcool aqueux plutôt que de chauffer en tube scellé à 150°; car une température élevée favorise l'hydrolyse du cyanure (9, 11).

Cette réaction fournit, en plus de l'acide attendu, des produits neutres (insolubles en milieu alcalin) et des produits acides (insolubles en milieu neutre ou acide), dont les uns ou les autres prédominent suivant la nature des substituants dans le cycle du benzène (10).

### I. RÉACTION AVEC LE *p*-CHLORONITROBENZÈNE (Tableau I)

Suivant les indications de Bunnett (9), nous avons isolé, à partir du *p*-chloronitrobenzène, 10% de produits neutres (A), 37% d'acide *m*-chlorobenzoïque et 12% d'autres produits acides (B). Nous avons réussi à obtenir proportionnellement plus d'acide *m*-chlorobenzoïque et de produits B en modifiant la façon de les isoler.

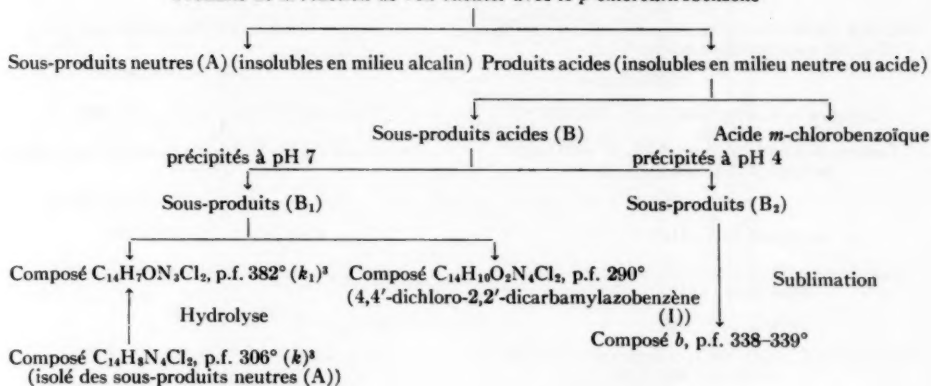
Une fois les produits A essorés, le filtrat est acidifié et les produits acides sont isolés et extraits à la ligroïne dans un Soxhlet. Seul l'acide *m*-chlorobenzoïque se dissout. Les produits B constituent le résidu. Ils peuvent être dissous dans de la soude diluée contenant un peu d'éthanol et séparés en deux groupes de composés: les premiers (B<sub>1</sub>) précipitent à pH 7 et les seconds (B<sub>2</sub>), à pH 4. Le même résultat est atteint, si les substances B<sub>1</sub>

<sup>1</sup>Manuscrit reçu le 21 septembre 1960.

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<sup>2</sup>Bénéficiaire de bourses d'études accordées par le Conseil national de Recherches du Canada, les firmes C.I.L. et Shell Oil et l'Office de Recherches scientifiques de la Province de Québec.

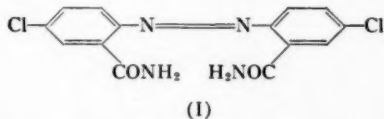
TABLEAU I

Produits de la réaction de von Richter avec le *p*-chloronitrobenzène

sont d'abord précipités dans le filtrat à pH 7, et ensuite les composés  $B_2$  à pH 4. L'acide *m*-chlorobenzoïque est alors obtenu de ces derniers par extraction à la ligroïne.

#### Nature des produits $B_1$ et $B_2$

Du mélange de produits  $B_1$  nous avons isolé deux substances. La première,  $C_{14}H_7ON_2Cl_2$ , fond à 382°. D'après un point de fusion mixte et les spectres infrarouges, elle s'est avérée identique à un composé ( $k_1$ ) obtenu par l'hydrolyse d'une substance ( $k$ ), p.f. 306°, qui appartient au groupe des produits neutres (A) de la réaction.<sup>3</sup> La seconde fond à 290° et a pour formule empirique  $C_{14}H_{10}O_2N_4Cl_2$ . Elle possède une fonction azoïque et un groupe amide. Nous sommes d'avis qu'elle est le 4,4'-dichloro-2,2'-dicarbamylazobenzène (I). Bunnett et Rauhut (12) ont récemment isolé une substance analogue, le 4,4'-diméthoxy-2,2'-dicarbamylazoxybenzène, à partir du *p*-nitroanisole.



Après avoir extrait l'acide *m*-chlorobenzoïque, nous avons sublimé, sous 12 mm de pression, le résidu des produits acides ( $B_2$ ). Le sublimé, recueilli entre 180 et 350°, se dissout dans le  $\beta$ -éthoxyéthanol bouillant et fournit par cristallisation une substance ( $b$ ) de point de fusion de 338-339°. Nous avons tenté de séparer le sublimé par sublimation fractionnée. Trois fractions ont été recueillies entre 180 et 210°, 210 et 290° et 290 et 350°. La troisième fraction contient la substance ( $b$ ), qui est évidemment un produit de transformation, puisqu'elle n'est plus soluble dans la soude diluée. Quant aux fractions 1 et 2, il a été impossible de les purifier.

#### Identification du composé $b$ (Tableau II)

D'après son analyse élémentaire, le composé  $b$ , p.f. 338-339°, possède la formule brute  $C_{14}H_6O_2N_2Cl_2$ . Il est insoluble dans les solvants organiques usuels ainsi que dans les

<sup>3</sup>La description de ces deux substances,  $k$  et  $k_1$ , et de leurs analogues  $k'$  et  $k'_1$ , paraîtra bientôt dans ce journal.

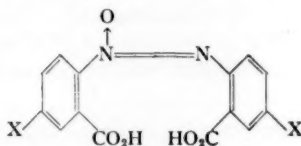


TABLEAU II  
Réactions qui ont conduit à l'identification du composé *b*

Acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique (II) (un des sous-produits acides B <sub>2</sub> )	Acide azoxybenzène-2,2'-dicarboxylique (III)
↓ Sublimation	↓ Sublimation
Composé <i>b</i> , C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> Cl <sub>2</sub> , p.f. 338-339° ou lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazolyl-(2)]-benzoïque (IX)	Composé <i>b'</i> , C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> , p.f. 292° ou lactone de l'acide 2-[3-oxyindazolyl-(2)]-benzoïque (VIII)
↓ NaOH alcoolique	↓ NaOH alcoolique
Composé <i>b</i> <sub>1</sub> , C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> Cl <sub>2</sub> ou acide 5-chloro-2-[5-chloro-3-oxy-indazolyl-(2)]-benzoïque (VII)	Composé <i>b'</i> <sub>1</sub> , C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> N <sub>2</sub> ou acide 2-[3-oxyindazolyl-(2)]-benzoïque (VI)
↓ HNO <sub>3</sub> [O]	↓ HNO <sub>3</sub> [O]
Composé <i>b</i> <sub>2</sub> , C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> N <sub>2</sub> Cl <sub>2</sub> , noircit vers 278-280° et fond à 308-310° ou acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique (V)	Composé <i>b'</i> <sub>2</sub> , C <sub>14</sub> H <sub>8</sub> O <sub>4</sub> N <sub>2</sub> , p.f. 237° ou acide azobenzène-2,2'-dicarboxylique (IV) (14)
↓ Chaleur	↓ Chaleur
Composé <i>b</i>	Composé <i>b'</i>

alcalis et les acides dilués, mais soluble dans la potasse alcoolique et l'acide sulfurique concentré dans lequel il précipite par addition d'eau.

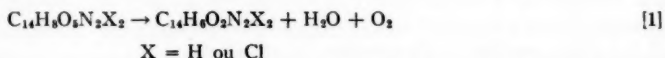
Nous nous sommes rendus compte que cette substance résulte d'une transformation de l'acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique (II) qui se produit au cours de sa sublimation. Désirant vérifier comment cet acide se comporte, lorsqu'il est soumis aux conditions de la réaction de von Richter,<sup>4</sup> nous l'avons synthétisé suivant la méthode utilisée (13) pour préparer l'acide non-chloré III correspondant. Nous avons constaté que, lorsqu'il est sublimé, il se transforme en la substance *b*, comme le révélant un point de fusion mixte et les spectres infrarouges (Fig. 1).



(II) X = Cl

(III) X = H

Au cours de cette transformation, l'acide perd une molécule d'eau et une molécule d'oxygène (équation 1, X = Cl).



Les bandes dues à l'absorption des groupes carboxyliques à 3050-2550, à 1420 et 1300 cm<sup>-1</sup> dans le spectre infrarouge de l'acide n'apparaissent pas dans celui du composé *b*, qui toutefois montre, à 1700 cm<sup>-1</sup>, la bande due à la présence du groupe carbonyle.

<sup>4</sup>Il ne change pas.

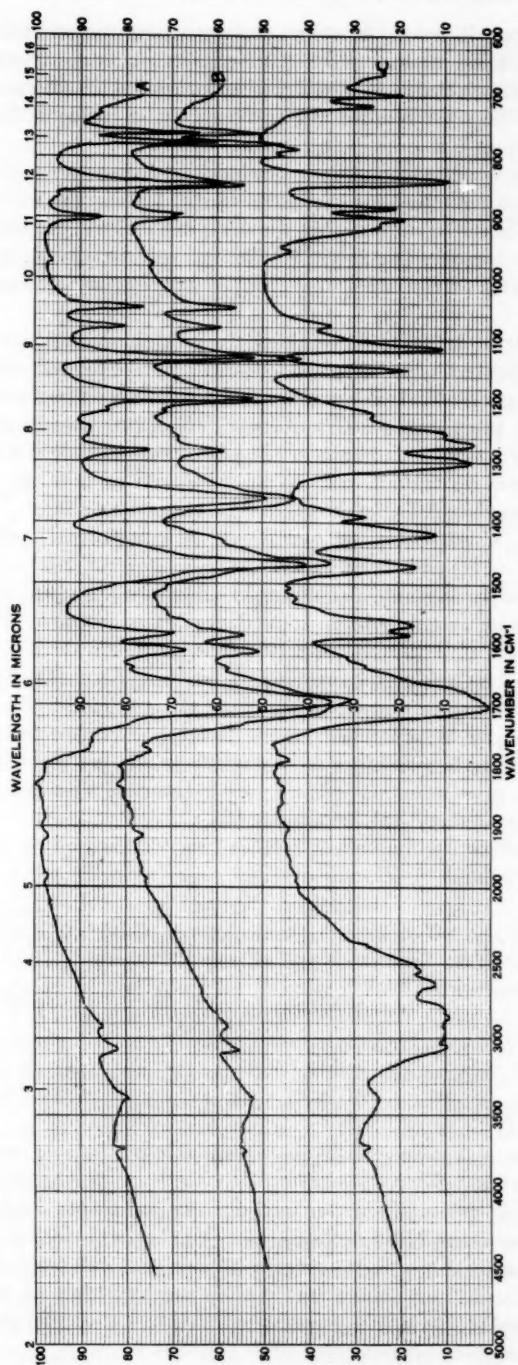


FIG. 1. Spectres infrarouges. (A) Lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazol-(2)]-benzoïque obtenue par sublimation de l'acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique. (B) Lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazol-(2)]-benzoïque obtenue par sublimation des produits B<sub>2</sub> provenant de la réaction de von Richter avec le *p*-chloronitrobenzène. (C) Acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique.

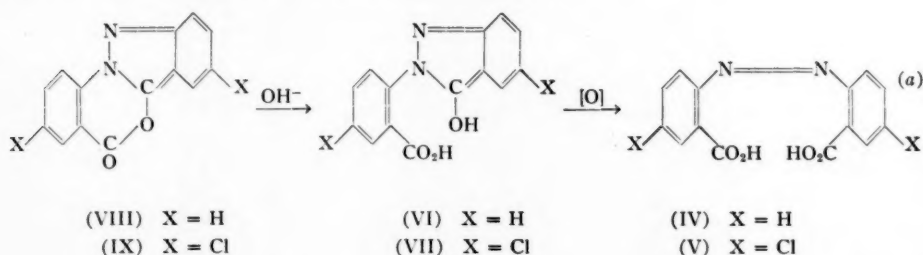
La substance *b* ne possède pas de fonction azoïque, azoxyque, nitrée, amine tertiaire ou amide secondaire. Elle donne le test des 1,2-dicétones, mais n'est pas oxydée par un mélange de peroxyde d'hydrogène et d'acide perchlorique et ne se condense pas avec l'*o*-phénylènediamine. Elle n'est réduite ni par l'étain ou le fer en milieu acide, ni par l'hydrogène et le palladium à la pression atmosphérique.

Par ébullition dans la soude alcoolique, le composé *b* se transforme en une substance blanche (*b*<sub>1</sub>) qui est très soluble dans la soude diluée. Le spectre infrarouge de cette dernière présente les caractéristiques des dimères des acides carboxyliques (bande d'absorption due au groupement carbonyle à 1728 cm<sup>-1</sup> et, dans la région de 3100–2400 cm<sup>-1</sup>, une série de bandes attribuables aux groupes hydroxyles fortement associés par ponts hydrogène).

L'analyse centésimale et le poids moléculaire du produit de saponification *b*<sub>1</sub> correspondent à la formule brute C<sub>14</sub>H<sub>8</sub>O<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub>. Celle-ci ne diffère de celle de la substance *b* que par les éléments d'une molécule d'eau en plus. La substance *b*<sub>1</sub> est oxydée par l'acide nitrique en un produit jaune-orangé, C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub>Cl<sub>2</sub> (*b*<sub>2</sub>), qui noircit vers 278–281° et fond à 308–310°. Sous l'action de la chaleur, elle perd une molécule d'eau et redonne la substance *b*. À ce stade-ci du travail, nous avons poursuivi cette étude de structure en utilisant l'acide azoxybenzène-2,2'-dicarboxylique (III) correspondant.

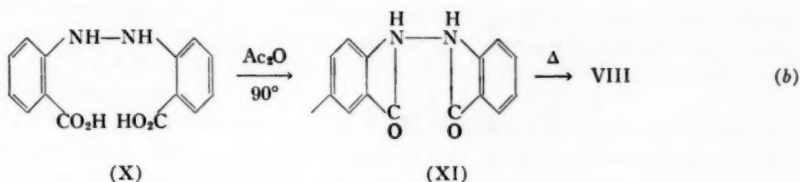
Cet acide non-chloré, C<sub>14</sub>H<sub>10</sub>O<sub>5</sub>N<sub>2</sub>, tel que prévu, se transforme facilement par sublimation (équation 1, X = H) en la substance C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub> (*b*'), p.f. 292°, qui est l'analogue du composé *b*. Saponifiée par la soude alcoolique, la substance *b*' donne un composé blanc, C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub> (*b*<sub>1</sub>'), analogue au composé *b*<sub>1</sub>. L'oxydation du composé *b*<sub>1</sub>' à l'acide nitrique donne un produit orangé, C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub> (*b*<sub>2</sub>'), de point de fusion de 237°, analogue à la substance *b*<sub>2</sub> et identique à l'acide azobenzène-2,2'-dicarboxylique (IV) (14).

Carré (15, 16) a synthétisé ce dernier acide en oxydant l'acide 2-[3-oxy-indazyl-(2)]-benzoïque (VI), obtenu par la saponification de la lactone correspondante (VIII) (a). Or toutes les propriétés de la substance *b*' montrent qu'elle est identique à la lactone VIII (17). Par analogie, nous pouvons conclure que le composé *b* est la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (IX).

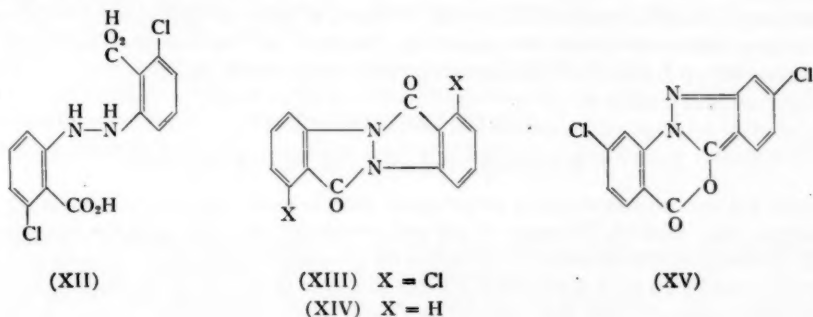


D'ailleurs, le produit *b*<sub>1</sub>, qui provient de la saponification de la substance *b*, doit nécessairement être l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (VII); car, le composé jaune-orangé (*b*<sub>2</sub>) qu'il donne, lorsqu'il est oxydé par l'acide nitrique, est l'acide 4,4'-dichlorazobenzène-2,2'-dicarboxylique (V) de point de fusion de 308–310°. En effet, un point de fusion mixte et les spectres infrarouges ont montré que ce dernier acide est identique à l'acide que nous avons obtenu par synthèse, en réduisant l'acide 2-nitro-5-chlorobenzoïque par le zinc et la soude en l'acide 4,4'-dichlorohydrazobenzène-2,2'-dicarboxylique et oxydant celui-ci par l'acide nitrique.

Diverses opinions ont été émises concernant la structure de composés du genre de la lactone VIII. Celle-ci peut être obtenue par la déshydratation de l'acide hydrazobenzène-2,2'-dicarboxylique (X). D'après Heller (18), cette réaction se ferait par l'intermédiaire du bisanthranile (XI) (b).



Reich et Merki (19) ont, par ailleurs, transformé le 2-nitro-6-chlorobenzaldéhyde en l'acide 3,3'-dichlorohydrazobenzène-2,2'-dicarboxylique (XII) et, celui-ci en une substance de point de fusion de 347-348°, insoluble dans les acides et les bases, à laquelle ils attribuent la structure dilactame XIII.



D'autre part, par déshydratation de l'acide 5,5'-dichlorohydrazobenzène-2,2'-dicarboxylique, Heller (18) a obtenu un isomère de la substance XIII, fondant à 335°, et lui attribue la structure XV.

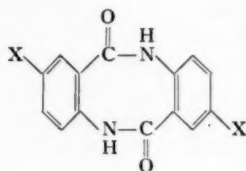
Enfin, à la suite d'une étude des spectres infrarouges du bisanthranile XI de Heller et de la lactone VIII, Mosby (20) prétend qu'il faudrait attribuer au bisanthranile la structure lactone VIII et à la supposée lactone VIII, la structure dilactame XIV.

Nous sommes d'avis que la saponification des substances *b* et *b'* en acides 2-[3-oxy-indazyl-(2)]-benzoïques VII et VI justifie une structure lactone, mais non dilactame. En effet, l'obtention de ces acides VI et VII par la saponification des dilactames XIV et XIII ne pourrait s'expliquer que par une transformation facile des acides hydrazobenzène-2,2'-dicarboxyliques en acides 2-[3-oxy-indazyl-(2)]-benzoïques. Dans ce cas cette transformation devrait alors se produire en premier lieu au moment de la cyclisation au lieu de la transformation en dilactame.

Au cours de cette étude, nous avons voulu synthétiser la 2,9-dichlorophénomazine XVI. Selon Cooper et Partridge (21), l'anthranilate de méthyle se condense en présence de sodium métallique et de benzonitrile pour donner la phénomazine (XVII) et un peu de 4-hydroxy-2-phénylquinazoline (XVIII).

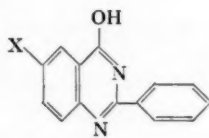
Le 5-chloroanthranilate de méthyle peut être préparé en chlorurant l'anthranilate de méthyle (22) ou en estérifiant l'acide 5-chloroanthranilique (23). Nous l'avons obtenu

en réduisant le 2-nitro-5-chlorobenzoate de méthyle par le fer activé. Le 5-chloro-anthranilate de méthyle se condense dans le xylène en présence de benzonitrile et de sodium métallique; mais nous n'avons isolé que de la 6-chloro-2-phényl-4-hydroxyquinazoline (XIX).



(XVI) X = Cl

(XVII) X = H



(XVIII) X = H

(XIX) X = Cl

## II. RÉACTION AVEC LE NITROBENZÈNE

La réaction de von Richter avec le nitrobenzène a fourni de l'acide benzoïque et une substance,  $C_{14}H_9ON_3$ , fondant à 334–336°. D'après un point de fusion mixte et les spectres infrarouges, elle s'est avérée identique à un composé ( $k'$ ) obtenu par l'hydrolyse d'une substance ( $k'$ ), p.f. 222–223°, qui est un produit neutre de la réaction.<sup>3</sup>

### PARTIE EXPÉRIMENTALE<sup>3</sup>

#### I. RÉACTION AVEC LE *p*-CHLORONITROBENZÈNE

En ce qui concerne la réaction proprement dite, le mode opératoire suivi est, à peu de variantes près, celui de Bunnett et ses collaborateurs (9). Une solution comprenant 1 partie de *p*-chloronitrobenzène et 4 parties de cyanure de potassium dans 10 parties (en volume) d'éthanol à 50% est bouillie à reflux pendant 48 heures. Le produit de la réaction est ensuite étendu à cinq fois son volume avec de l'eau et filtré. (Avant de filtrer, le mélange peut être soumis à une distillation à la vapeur d'eau. Celle-ci permet de récupérer environ 1% de la quantité initiale de *p*-chloronitrobenzène, qui est rapidement entraînée par la vapeur, et d'améliorer de 10% le rendement en acide *m*-chlorobenzoïque.) On obtient ainsi un solide neutre A jaune-verdâtre et un filtrat A.

##### (1) Isolement de l'acide *m*-chlorobenzoïque

L'acide *m*-chlorobenzoïque peut être extrait du filtrat A selon la méthode de Bunnett (8) ou suivant la modification suivante. Le filtrat A est acidifié à pH 4 et maintenu à 5° pendant au moins 12 heures. Les acides précipités sont alors filtrés et lavés à l'eau. Le filtrat et les eaux de lavage sont extraits au chloroforme et les extraits chloroformés épuisés à la soude 5%. La solution alcaline est chauffée pour en chasser les traces de chloroforme, puis est refroidie et acidifiée. Les acides ainsi précipités sont essorés, ajoutés aux acides déjà isolés, séchés sous pression réduite et extraits à la ligroïne (Eb = 65–110°) dans un Soxhlet. Seul l'acide *m*-chlorobenzoïque est extrait. L'extrait est ensuite évaporé à siccité. Le résidu, cristallisé dans le même solvant, fournit l'acide *m*-chlorobenzoïque (rendement 46% de la théorie) de point de fusion de 155–157°.

<sup>3</sup>Les points de fusion (p.f.) ont été pris en tubes capillaires et ne sont pas corrigés. Les spectres infrarouges ont été déterminés au moyen d'un spectromètre Beckman IR4; les solides étaient mélangés à du bromure de potassium et pressés; seules les bandes servant à l'identification des composés sont indiquées: les valeurs en  $cm^{-1}$  correspondent au maximum d'absorption, sauf celles qui correspondent aux groupes hydroxyles des acides carboxyliques et qui montrent la région entière de l'absorption. Les microanalyses ont été effectuées par M. W. Manser, Zürich, Suisse.



(2) *Isolement et identification d'autres produits*

Du filtrat A, en plus de l'acide *m*-chlorobenzoïque, on peut isoler des produits (B) qui précipitent à différents pH.

(a) *À pH 7*

En ajoutant lentement au filtrat A, refroidi dans un bain glacé, de l'acide chlorhydrique 6 *N* jusqu'à ce que le pH devienne 5, puis la quantité de carbonate de sodium nécessaire pour le ramener à 7, des produits (B<sub>1</sub>) (10 à 15% du poids de *m*-chloronitrobenzène de départ) précipitent et sont filtrés.

*4,4'-Dichloro-2,2'-dicarbamylazobenzène (I) et 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (k<sub>1</sub>).*— Les produits B<sub>1</sub> (5.56 g), sublimés, sous 12 mm de mercure entre 180 et 350°, donnent un sublimé jaune-orangé (1.5 g). Lorsque celui-ci est sublimé de nouveau sous pression réduite, on recueille deux portions, l'une (0.386 g) au-dessous, et l'autre (0.919 g) au-dessus de 200°. Cette dernière peut être séparée en deux autres fractions par une troisième sublimation. Le composé qui constitue la première fraction est recueilli au-dessous de 220° et fond à 290°. D'après son analyse élémentaire et ses propriétés, il serait le 4,4'-dichloro-2,2'-dicarbamylazobenzène (I). Calculé pour C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 49.87%; H, 2.99%; N, 16.62%. Trouvé: C, 50.09%; H, 2.64%; N, 16.85%. Le produit de la deuxième fraction, recueilli entre 250 et 350°, cristallise dans la *N,N*-diméthylformamide en aiguilles de couleur jaune pâle et de point de fusion de 382°. Un point de fusion mixte de cette substance et du composé *k*<sub>1</sub> (le produit d'hydrolyse d'une substance *k* qui appartient aux produits neutres (A) de la réaction) n'est pas abaissé et les spectres infrarouges des deux sont identiques. Cette substance est le 3,8-dichloro-6-céto-quinazolo[1,2,2',3']indazol.

(b) *À pH 4*

En portant à 4 le pH du filtrat obtenu en (a) et en procédant de la façon qui est décrite précédemment pour l'extraction de l'acide *m*-chlorobenzoïque à la ligroïne, d'autres produits acides (B<sub>2</sub>) ont été isolés. Le résidu de l'extraction à la ligroïne (Eb = 65–110°) constitue ces produits.

*Lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (IX) (b).*— Tout comme les produits B<sub>1</sub>, les produits B<sub>2</sub> (18–20% du poids de *p*-chloronitrobenzène de départ) n'ont pu être séparés que par sublimation. Trois températures ont été arbitrairement choisies pour recueillir trois fractions: (i) au-dessous de 200°, (ii) entre 210 et 240° et (iii) au-dessus de 250°. Il a été impossible de purifier les deux premières substances, soit par cristallisation, soit par sublimation. Le premier composé (i) fond à 205–210°. Calculé pour C<sub>14</sub>H<sub>6</sub>O<sub>7</sub>N<sub>4</sub>Cl<sub>2</sub>: C, 39.54%; H, 4.27%; N, 13.18%. Trouvé: C, 39.70%; H, 4.15%; N, 13.03%. Le second fond à 280–290°. Calculé pour C<sub>14</sub>H<sub>6</sub>O<sub>8</sub>N<sub>4</sub>Cl<sub>2</sub>: C, 51.45%; H, 2.59%; N, 12.00%. Trouvé: C, 51.88%; H, 2.53%; N, 11.60%. Quant à la troisième substance (iii), elle est la plus abondante des trois et correspond à la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque. Elle cristallise dans le  $\beta$ -éthoxyéthanol ou la 3-pentanone en paillettes lustrées de point de fusion 338–339°. Calculé pour C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>N<sub>4</sub>Cl<sub>2</sub>: C, 55.11%; H, 1.98%; N, 9.18%. Trouvé: C, 55.02%; H, 2.14%; N, 9.32%. L'acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique (0.100 g), dont la synthèse apparaît plus loin, se sublime sous 12 mm de mercure, entre 250 et 350°, pour donner la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (0.053 g) qui, après cristallisation dans le  $\beta$ -éthoxyéthanol, fond à 338°. Un point de fusion mixte d'un mélange de ce composé et de la substance (iii), décrite précédemment, n'est pas abaissé et les spectres infrarouges des deux sont identiques (Fig. 1). Calculé

pour  $C_{14}H_6O_2N_2Cl_2$ : C, 55.11%; H, 1.98%; O, 10.42%; N, 9.18%; Cl, 23.24%. Trouvé: C, 54.70%; H, 2.32%; O, 10.42%; N, 9.18%; Cl, 22.96%. Les essais de synthèse de l'acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique à partir de l'acide 5-chloro-2-nitrobenzoïque (4.0 g) selon la méthode utilisée pour la préparation de l'acide 4,4'-diméthoxyazoxybenzène-2,2'-dicarboxylique (12) ou pour celle de l'acide azoxybenzène-2,2'-dicarboxylique (24) n'ont pas permis d'obtenir l'acide à l'état pur par la cristallisation des produits engendrés. Toutefois, en sublimant ces derniers sous 12 mm de mercure, on recueille, au-dessous de 200°, de l'acide 5-chloroanthranilique (p.f. 213–214°), et, entre 210 et 350°, un sublimé qui cristallise dans le  $\beta$ -éthoxyéthanol en paillettes lustrées de couleur jaune pâle et de point de fusion de 338–339°. Ce dernier est la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (b) identique à la substance (iii). Calculé pour  $C_{14}H_6O_2N_2Cl_2$ : N, 9.18%. Trouvé: N, 9.11%.

*Acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (VII) (b<sub>1</sub>).*—De la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (b) (0.030 g), dissoute dans 3 ml de soude 5 N et 3 ml d'éthanol, est chauffée à reflux pendant 2 heures. On dilue ensuite par l'eau à 25 ml et acidifie par l'acide chlorhydrique. L'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque précipite. Il cristallise dans l'acide acétique à 80% en lamelles blanches. Spectre infrarouge: —OH(—COOH), 2400–3400  $cm^{-1}$ ; =CO acide, 1730  $cm^{-1}$ . Chauffé au-dessus de 100°, il redonne lentement la lactone de départ. Calculé pour  $C_{14}H_6O_3N_2Cl_2$ : C, 52.03%; H, 2.49%; N, 8.67%. Trouvé: C, 52.18%; H, 2.37%; N, 8.81%.

*Acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique (II).*—Un mélange d'acide 2-nitro-5-chlorobenzoïque (5.0 g), d'hydroxyde de potassium (5.0 g) et d'éthanol (20 ml) est chauffé au bain-marie durant 2 heures et ensuite évaporé à siccité. Le résidu est dilué par l'eau, refroidi par addition de glace et acidifié par l'acide chlorhydrique. L'acide précipité est agité pendant environ 15 minutes avec 300 ml d'eau de baryte. On filtre, fait barboter un courant d'anhydride carbonique dans le filtrat pour précipiter l'excès de baryte et filtre de nouveau. En acidifiant le filtrat, l'acide 4,4'-dichloroazoxybenzène-2,2'-dicarboxylique (1.62 g, 36% de la théorie) précipite. Il cristallise dans l'acide acétique en courtes aiguilles de point de fusion de 272° (avec décomposition). Calculé pour  $C_{14}H_6O_5N_2Cl_2$ : C, 47.36%; H, 2.27%; N, 7.88%; Cl, 19.96%. Trouvé: C, 47.31%; H, 2.21%; N, 7.67%; Cl, 19.88%.

*Acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique (V) (b<sub>2</sub>).*—À une solution de 0.21 g de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque dans 30 ml de soude à 2%, on ajoute 30 ml d'acide nitrique concentré et chauffe au bain-marie pendant 2 heures. Après un repos de quelques minutes à la température ambiante, on filtre, lave à l'eau et sèche le précipité qui s'est formé. L'acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique cristallise dans l'éthanol en fines aiguilles jaunes qui noircissent vers 278–280° et fondent à 308–310°. Calculé pour  $C_{14}H_6O_4N_2Cl_2$ : C, 49.57%; H, 2.38%; N, 8.26%. Trouvé: C, 49.46%; H, 2.59%; N, 8.55%. Un point de fusion mixte de cette substance et de l'acide obtenu par synthèse de la façon décrite ci-après n'est pas abaissé. Les spectres infrarouges de l'acide provenant des deux sources différentes sont de plus identiques.

On dissout 4.65 g d'acide 2-nitro-5-chlorobenzoïque dans 30 ml d'éthanol, ajoute à cette solution 6 ml de soude à 50% et chauffe au bain-marie. Sous agitation mécanique, on introduit ensuite peu à peu du zinc en poudre jusqu'à ce que la solution de rouge sombre passe au rouge pâle (environ 2 heures). Après un repos de quelques minutes, le mélange est filtré et le précipité d'oxyde de zinc ainsi que l'excès de zinc est lavé par de

l'éthanol bouillant. Le filtrat est réuni à l'éthanol de lavage, dilué par un égal volume d'eau et acidifié par de l'acide chlorhydrique concentré. Le précipité jaune pâle, qui se forme, est essoré, lavé à l'eau et séché. On dissout ensuite ce solide (1.15 g) dans 280 ml d'acide acétique bouillant, ajoute 15 ml d'acide nitrique concentré à la solution et la fait bouillir à reflux pendant quelques minutes. À la température ambiante l'acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique cristallise en aiguilles jaune-orangé. Après deux cristallisations dans l'acide acétique, il noircit vers 278–280° et fond à 308–310°. Calculé pour  $C_{14}H_8O_4N_2Cl_2$ : C, 49.57%; H, 2.38%; N, 8.26%. Trouvé: C, 49.31%; H, 2.51%; N, 8.42%.

*4-Hydroxy-6-chloro-2-phénylquinazoline (XIX).*—Le 5-chloro-2-nitrobenzoate de méthyle (12) est réduit en 5-chloroanthranilate de méthyle par le fer activé dans le benzène humide selon la méthode générale de Hazlet et Dornfeld (25) avec un rendement de 91%. On introduit ensuite, sous agitation mécanique, 5.0 g de 5-chloroanthranilate de méthyle et 4.2 g de benzonitrile dans un ballon muni d'un réfrigérant et contenant 1.2 g de sodium pulvérisé dans 125 ml de xylène anhydre. Une réaction exothermique s'amorce immédiatement. Une fois celle-ci atténuée (environ une demi-heure), on chauffe à reflux pendant 2 heures et on extrait ensuite à la soude 5 N le produit de la réaction. En acidifiant la solution alcaline, on obtient la 4-hydroxy-6-chloro-2-phénylquinazoline qui cristallise dans le xylène contenant un peu d'éthanol. Son point de fusion est de 292° et le rendement de 1.97 g (27% de la théorie). Calculé pour  $C_{14}H_9ON_2Cl$ : C, 65.41%; H, 3.54%; N, 10.94%. Trouvé: C, 65.00%; H, 3.53%; N, 10.90%.

*Lactone de l'acide 2-[3-oxy-indazyl-(2)]-benzoïque (VIII) (b').*—L'acide azoxybenzène-2,2'-dicarboxylique se transforme par sublimation en la lactone de l'acide indazylbenzoïque. Sous 12 mm de mercure, lorsque la température du bain atteint 160°, l'acide ramollit, se gonfle et se solidifie de nouveau vers 200°. Il faut alors discontinuer l'opération et pulvériser la masse avant de continuer. Au-dessus de 280°, la sublimation se fait assez rapidement. À partir de 2.0 g de l'acide, on obtient 0.71 g de la lactone de l'acide 2-[3-oxy-indazyl-(2)]-benzoïque. Elle cristallise dans la 3-pentanone ou le  $\beta$ -éthoxy-éthanol en pailettes lustrées de couleur jaune pâle et fond à 292° (p.f. lit. 294° (16)). Calculé pour  $C_{14}H_8O_2N_2$ : C, 71.18%; H, 3.14%; N, 11.86%. Trouvé: C, 71.02%; H, 3.42%; N, 11.76%.

*Acide 2-[3-oxy-indazyl-(2)]-benzoïque (VI) et acide azobenzène-2,2'-dicarboxylique (IV) (b<sub>1</sub>').*—L'acide 2-[3-oxy-indazyl-(2)]-benzoïque est obtenu en faisant bouillir à reflux une suspension de 0.5 g de la lactone de l'acide 2-[3-oxy-indazyl-(2)]-benzoïque (obtenu précédemment par sublimation) dans 30 ml de soude 5 N et 30 ml d'éthanol. L'acide isolé (0.49 g) cristallise dans l'eau en lamelles blanches et fond à environ 285° après ramollissement vers 230° (p.f. lit. 230° (16)). De l'acide 2-[3-oxy-indazyl-(2)]-benzoïque (0.4 g) dissous dans la soude à 2% (40 ml) est oxydé par l'acide nitrique concentré (40 ml), comme il est décrit précédemment pour l'acide 4,4'-dichloroazobenzène-2,2'-dicarboxylique. L'acide azobenzène-2,2'-dicarboxylique obtenu cristallise dans l'eau et fond à 237° avec décomposition.

## II. RÉACTION AVEC LE NITROBENZÈNE

Un mélange de 20.0 g de nitrobenzène, de 60.0 g de cyanure de potassium et de 200 ml de glycol à 90% est bouilli à reflux pendant 3 heures et abandonné à la température ambiante pendant 15 heures. En diluant avec de l'eau à environ 3000 ml, tout comme

dans le cas de la réaction avec le *p*-chloronitrobenzène, on obtient un solide neutre A' jaune-verdâtre et un filtrat A'.

L'acide benzoïque (20% de la théorie) est extrait du filtrat A' en procédant exactement tel que décrit précédemment pour l'acide *m*-chlorobenzoïque. Le résidu de l'extraction à la ligroïne (Eb = 65–110°) contient le produit acide B'.

#### *Isolement et identification du produit acide B'*

Le solide B', obtenu précédemment après l'extraction de l'acide benzoïque à la ligroïne, ne se sublime qu'au-delà de 250°, sous 12 mm de mercure. Le sublimé ne correspond pas à la lactone de l'acide 2-[3-oxy-indazyl-(2)]-benzoïque, mais bien au 6-cétoquinazolo-[1,2,2',3']-indazol.<sup>3</sup> En effet, cristallisé dans l'acide acétique, il fond à 334–336°. Un point de fusion mixte de cette substance et du composé *k*<sub>1</sub>' (le produit d'hydrolyse d'une substance *k*', un produit neutre de la réaction) n'est pas abaissé. Calculé pour C<sub>14</sub>H<sub>9</sub>ON<sub>3</sub>: C, 71.48%; H, 3.85%; N, 17.86%. Trouvé: C, 71.39%; H, 4.14%; N, 17.78%.

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## CONTRIBUTION À L'ÉTUDE DE LA RÉACTION DE VON RICHTER

### II. SUR L'IDENTIFICATION DE PRODUITS NEUTRES<sup>1</sup>

E. CULLEN<sup>2</sup> ET PH. L'ÉCUEYER

#### RÉSUMÉ

La réaction de von Richter fournit, en plus de produits acides, des composés neutres. Avec le *p*-chloronitrobenzène, elle donne le 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol et le 4,4'-dichloro-2-carbamylazoxybenzène, et avec le nitrobenzène, le 6-iminoquinazolo[1,2,2',3']indazol.

La réaction de von Richter fournit, outre l'acide attendu, des produits neutres et des produits acides. Nous avons décrit précédemment (1) deux de ces derniers formés par la réduction du groupement nitré. Dans le présent mémoire nous décrivons trois produits neutres. Deux proviennent de la réaction avec le *p*-chloronitrobenzène et l'autre, de la réaction avec le nitrobenzène. En extrayant à la butanone les produits bruts neutres (A), essorés après la réaction avec le *p*-chloronitrobenzène, nous avons isolé trois substances, *k*, *m* et *n* (cette dernière en traces seulement), fondant respectivement à 306, 422 et 228-229°. L'extraction du filtrat (A) fournit même des traces d'un quatrième composé de point de fusion 164°.

La substance *k* est insoluble dans les bases et les acides dilués, mais se dissout dans l'acide sulfurique concentré. Elle est presque insoluble dans l'éther et peu soluble dans les autres solvants organiques usuels. En solution dans l'éthanol ou la butanone elle exhibe une forte fluorescence jaune-verdâtre. Son analyse élémentaire et la détermination de son poids moléculaire ont permis de déduire la formule empirique  $C_{14}H_8N_4Cl_2$ . Elle forme un chlorhydrate,  $C_{14}H_8N_4Cl_2 \cdot HCl$ , qui fond avec décomposition à 300-310°, et un dérivé acétylé,  $C_{16}H_{10}ON_4Cl_2 \cdot \frac{1}{2}(CH_3CO)_2O$ , de point de fusion de 260-261°.

Cette substance *k* est hydrolysée par l'acide chlorhydrique concentré en solution acétique et saponifiée par les bases inorganiques dans le glycol en libérant de l'ammoniac. Son produit d'hydrolyse (*k*<sub>1</sub>) est insoluble dans les bases et les acides dilués, presque insoluble dans les solvants organiques, mais soluble à chaud dans les acides concentrés et la potasse alcoolique. Une fois sublimé, il fond à 378-380°. Son analyse centésimale correspond à la formule brute  $C_{14}H_7ON_3Cl_2$ . Il forme un sel de potassium  $C_{14}H_6N_3Cl_2OK \cdot 2H_2O$ , fondant à 420-422° (cristallisé dans l'eau), ou  $C_{14}H_6N_3Cl_2OK \cdot H_2O$ , de point de fusion 410° (cristallisé dans l'isopropanol), un sel de baryum,  $(C_{14}H_6N_3Cl_2O)_2Ba \cdot 4H_2O$ , et un éther méthylique,  $C_{14}H_6N_3Cl_2OCH_3$ , de point de fusion de 278-279°, mais pas de dérivé acétylé.

Les deux composés, *k* et *k*<sub>1</sub>, donnent les tests des amines secondaires et des amides secondaires. Que le produit d'hydrolyse *k*<sub>1</sub> possède une fonction amide secondaire semble de plus confirmé par le fait qu'il forme une N-nitrozolactame dont l'hydrolyse donne le composé  $C_{14}H_8O_3N_4Cl_2$  de point de fusion de 418-420°.

Le spectre infrarouge de la substance *k* indique une fonction imine (absorption à 3325 et 1650  $cm^{-1}$ ) et celui de la substance *k*<sub>1</sub>, une fonction carbonyle (absorption à 1670  $cm^{-1}$ ), mais aucune vibration définie attribuable au groupe hydroxyle dans la région de 3500  $cm^{-1}$ . Il est évident que c'est la fonction imine de la substance *k* qui est acétylée;

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<sup>2</sup>Bénéficiaire de bourses d'études accordées par le Conseil national de Recherches du Canada, les firmes C.I.L. et Shell Oil et l'Office de Recherches scientifiques de la Province de Québec.



car, après l'élimination de cette fonction par hydrolyse, l'acétylation n'est plus possible.

La substance *k* n'est pas réduite par le fer activé, l'hydrogène en présence de palladium, ou l'hydruide de lithium et d'aluminium. Le composé *k* ou son dérivé acétylé est décomposé par l'acide chromique ou le permanganate neutre ou alcalin; mais il fournit, tout comme son produit d'hydrolyse *k*<sub>1</sub>, des composés définis, lorsqu'ils sont traités par le peroxyde d'hydrogène à 95% et l'acide perchlorique en milieu acétique. Dans le premier cas, la substance obtenue fond à 252–254° et a la formule brute C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>N<sub>4</sub>Cl<sub>2</sub>. Dans le second, le composé formé, de point de fusion de 266°, a la formule empirique C<sub>14</sub>H<sub>7</sub>O<sub>3</sub>N<sub>4</sub>Cl<sub>2</sub>.

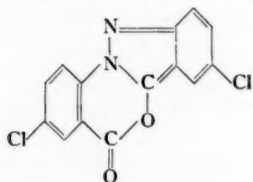
Ces deux produits d'oxydation, qui possèdent deux atomes d'oxygène de plus que les composés de départ, libèrent de l'iode dans une solution d'iodure de potassium à 10%. Ils se comportent comme des oxydes d'amines et seraient formés par l'oxydation de deux atomes d'azote tertiaire, laissant intactes la fonction amidine de la substance *k* et la fonction amide du composé *k*<sub>1</sub>; car, ils peuvent encore réagir avec les nitrites.

Par analogie avec la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazyl-(2)]-benzoïque (I) (1), nous suggérons la structure II pour la substance *k*, et la formule III pour son produit d'hydrolyse *k*<sub>1</sub>.

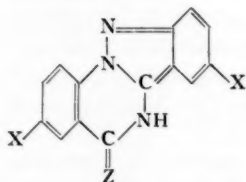
Nous avons aussi isolé parmi les produits neutres de la réaction de von Richter avec le nitrobenzène une substance *k'*, C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>, de point de fusion de 222–223°, analogue à la substance *k*. Par hydrolyse elle fournit un composé *k*<sub>1</sub>', C<sub>14</sub>H<sub>9</sub>ON<sub>3</sub>, analogue au composé *k*<sub>1</sub>.

Ces deux substances, *k'* et *k*<sub>1</sub>', sont relativement plus solubles dans les solvants organiques que leurs analogues chlorés, mais elles possèdent les mêmes propriétés chimiques et caractéristiques physiques. Ainsi, leurs solutions alcooliques montrent une forte fluorescence en lumière ultraviolette et les vibrations imine et carbonyle, qui apparaissent respectivement dans le spectre infrarouge des substances *k* et *k*<sub>1</sub>, se retrouvent aussi dans celui des composés *k'* et *k*<sub>1</sub>'. Nous suggérons les structures respectives IV et V pour ces substances *k'* et *k*<sub>1</sub>'.

La substance *k'* semble identique à celle que Pinnow et Müller (2) ont isolée parmi les produits de la réduction de l'*o*-nitrobenzonitrile et qui, d'après eux, serait la diphénylaminopyrodiadiazoline (VI). Les deux ont le même point de fusion, donnent le même chlorhydrate, le même dérivé acétylé, le même dérivé benzoylé et le même produit d'hydrolyse (VII, d'après Pinnow et Müller).



(I)

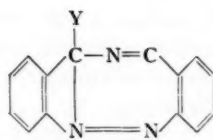


(II) X = Cl; Z = NH

(III) X = Cl; Z = O

(IV) X = H; Z = NH

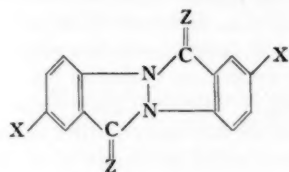
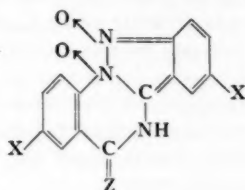
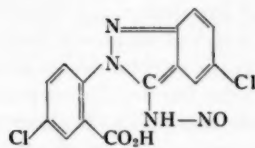
(V) X = H; Z = O

(VI) Y = NH<sub>2</sub>

(VII) Y = OH

À notre avis, les structures VI et VII proposées par Pinnow et Müller sont inacceptables; les tests indiquent la présence d'une fonction amidine, mais non celle d'une fonction amine primaire dans la molécule de la substance *k'*. D'ailleurs, les spectres infrarouges des substances *k* et *k'* excluent la présence d'une fonction amine primaire et

ceux de leurs produits d'hydrolyse,  $k_1$  et  $k'_1$ , celle d'un groupe hydroxyle. Il semble aussi impossible d'attribuer la structure VIII à la substance  $k$ ; car, si celle-ci possédait cette formule, elle aurait donné la dilactame correspondante IX, au lieu de la lactame que nous avons obtenue par hydrolyse. Nous proposons donc respectivement pour la substance  $k'$  et son produit d'hydrolyse  $k'_1$  les structures IV et V qui rendent bien compte de leurs spectres infrarouges et de leurs propriétés chimiques.

(VIII)  $X = Cl$ ;  $Z = NH$ (IX)  $X = Cl$ ;  $Z = O$ (X)  $X = Cl$ ;  $Z = NH$ (XI)  $X = Cl$ ;  $Z = O$ 

(XII)

Les substances  $k$  et  $k'$  seraient donc le 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol (II) et le 6-iminoquinazolo[1,2,2',3']indazol (IV), et leurs produits d'hydrolyse,  $k_1$  et  $k'_1$ , le 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (III), et le 6-cétoquinazolo[1,2,2',3']indazol (V).

Ajoutons que le comportement des deux substances,  $k$  et  $k'$ , vis-à-vis de l'oxydation et de la réduction ressemble à celui de l'indazol lui-même (3). C'est d'ailleurs aussi fort probablement à la présence du squelette de l'indazole qu'il faut attribuer la formation d'un produit rouge sous l'action de l'acide nitrique sur le composé d'hydrolyse  $k_1$  (réaction de Knorr (4)). De plus, il est connu que la 2,4-dicéto-6-tétrahydroquinazoline se forme facilement par chauffage de l'acide *o*-uraminobenzoïque dans la soude concentrée (5), qu'elle se sublime à haute température et forme des sels de sodium hydratés tout comme le composé  $k_1$ .

Les structures X et XI semblent acceptables pour les produits d'oxydation,  $C_{14}H_8O_2N_4Cl_2$  et  $C_{14}H_7O_2N_4Cl_2$ , de la substance  $k$  et de son produit d'hydrolyse  $k_1$ .

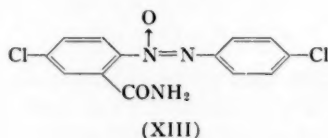
La substance  $C_{14}H_8O_2N_4Cl_2$ , qui est obtenue par nitrosation du produit d'hydrolyse  $k_1$ , pourrait avoir la structure XII, ce qui expliquerait sa solubilité dans la soude et ses caractéristiques d'amine secondaire. Son spectre infrarouge présente une forte vibration carbonyle à  $1700\text{ cm}^{-1}$ , alors que la large bande entre  $3200$  et  $2700\text{ cm}^{-1}$  du spectre du composé  $k_1$  est absente. Ceci laisse entendre que l'hydrogène de la fonction amine est vraiment substitué.

Enfin, l'allure identique de la courbe d'absorption de la substance  $k'$  et de celle de la lactone de l'acide 5-chloro-2-[5-chloro-3-oxy-indazol-(2)]-benzoïque (I) dans l'ultraviolet est conforme à la structure IV.

Il ne fait aucun doute que l'intermédiaire de la substance  $k$  est un produit de réduction du *p*-chloronitrobenzène, puisqu'une substance identique au produit non-chloré  $k'$  a été isolé par Pinnow et Müller (2) par réduction de l'*o*-nitrobenzonitrile. Toutefois, il est très peu probable que le nitrile soit un intermédiaire de la réaction de von Richter; car, après avoir fait bouillir pendant 20 heures une solution alcoolique de 2-nitro-5-chlorobenzonitrile dans les conditions de la réaction, nous n'avons pas obtenu le 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol (II).

Nous avons alors voulu vérifier si la substance *k'* pouvait être produite par la transformation du 2,2'-dicyanohydrazobenzène; il est, en effet, connu que l'acide hydrazobenzène-2,2'-dicarboxylique peut être transformé en la lactone de l'acide 2-[3-oxy-indazolyl-(2)]-benzoïque (6). En conséquence, nous avons traité le 2,2'-dicyanoazoxybenzène dans les conditions de la réaction de von Richter, et nous avons obtenu, probablement par l'intermédiaire du composé hydrazoïque, le 6-iminoquinazolo[1,2,2',3']-indazol (IV), comme l'ont confirmé un point de fusion mixte et les spectres infrarouges.

Le composé *n*, p.f. 228–229°, a la formule brute  $C_{13}H_9O_2N_3Cl_2$ . Il est insoluble dans les acides et les alcalis dilués et très peu soluble dans l'éther. Il donne le test du groupe azoxyque et celui des amides. Son spectre infrarouge ne montre aucune vibration nitrile, mais des bandes d'absorption correspondant à la déformation de valence d'une fonction amide secondaire. D'autre part, la seule bande d'absorption de son spectre ultraviolet indiquerait la fonction azoxyque (7). Ces données font croire que la substance *n* est le 4,4'-dichloro-2-carbamylazoxybenzène (XIII).



#### PARTIE EXPÉRIMENTALE<sup>3</sup>

Trois substances, *k*, *m* et *n*, peuvent être isolées du mélange de produits neutres (A) qui sont essorés une fois la réaction de von Richter avec le *p*-chloronitrobenzène terminée (1).

$(C_{30}H_{20}O_2N_{10}Cl_4)_n$  (*m*)

Le résidu (environ 2%), obtenu après l'extraction du solide neutre (A) à la butanone dans un Soxhlet, cristallise dans la N,N-diméthylformamide en aiguilles jaunes de point de fusion de 422–423°. Calculé pour  $(C_{30}H_{20}O_2N_{10}Cl_4)_n$ : C, 51.65%; H, 2.90%; N, 20.17%; Cl, 20.02%. Trouvé: C, 51.45%; H, 2.84%; N, 19.79%; Cl, 20.00%. Spectre ultraviolet: max  $\lambda_{\mu}$  234 ( $\epsilon$  38,800);  $\lambda_{\mu}$  245 ( $\epsilon$  38,200);  $\lambda_{\mu}$  315 ( $\epsilon$  11,560);  $\lambda_{\mu}$  420 ( $\epsilon$  4,400). Les valeurs de  $\epsilon$  sont calculées pour  $n = 1$ .

3,8-Dichloro-6-iminoquinazolo[1,2,2',3']indazol (*k*) (II)

L'extrait du solide (A) à la butanone est d'abord refroidi à 0°, puis porté à environ 50° et filtré, pour éliminer les dernières traces de la substance *m*. En refroidissant le filtrat, le 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol (environ 60–70% du solide (A)) cristallise sous forme de lamelles lustrées et transparentes de couleur jaune-verdâtre. Après deux cristallisations dans la butanone la substance fond à 306°. Calculé pour  $C_{14}H_8N_4Cl_2$ : C, 55.46%; H, 2.66%; N, 18.48%. Trouvé: C, 55.27%; H, 2.42%; N, 18.32%. Dans l'isopropanol elle cristallise en longues aiguilles transparentes, p.f. 307°, qui contiennent une demi-molécule de solvant de cristallisation. Calculé pour  $C_{14}H_8N_4Cl_2 \cdot \frac{1}{2}C_3H_8O$ : C, 55.86%; H, 3.63%; N, 16.82%; Cl, 21.28%; O, 2.40%. Trouvé: C, 55.46%; H, 3.48%; N, 16.90%; Cl, 20.82%; O, 2.36%. Spectre infrarouge: 1650, 3325 ( $=NH$ ), 3150  $cm^{-1}$  ( $-NH-$  associé).

<sup>3</sup>Les points de fusion (p.f.) ont été pris en tubes capillaires et ne sont pas corrigés. Les spectres ultraviolets ont été déterminés au moyen d'un spectromètre Beckman DU, en solution dans l'éthanol, et les spectres infrarouges, à l'aide d'un spectromètre Beckman IR-4; les solides étaient mélangés à du bromure de potassium et pressés; seules les bandes servant à l'identification des composés sont indiquées: les valeurs en  $cm^{-1}$  correspondent au maximum d'absorption, sauf celles qui correspondent au groupe  $=CO-NH-$  des amides secondaires qui montrent la région entière de l'absorption. Les microanalyses ont été effectuées par M. W. Manser, Zürich, Suisse.

La solution étherée de l'indazol II traitée à l'acide chlorhydrique gazeux forme facilement un chlorhydrate blanc, qui jaunit rapidement et fond avec décomposition entre 300 et 310°. Calculé pour  $C_{14}H_8N_4Cl_2 \cdot HCl$ : Cl, 30.77%. Trouvé: Cl, 29.50%. Spectre infrarouge: 1662 (NH·HCl), 2440 à 3050  $cm^{-1}$  (déplacement et élargissement) (8).

Le dérivé acétylé de l'indazol II est obtenu en faisant bouillir 50 mg de l'indazol dans 25 ml d'acide acétique, 0.5 ml de pyridine et 1 ml d'anhydride acétique et en cristallisant le produit dans l'acide acétique et ensuite le xylène. Il contient une demi-molécule d'anhydride acétique de cristallisation et fond à 260–261°. Calculé pour  $C_{16}H_{10}ON_4Cl_2 \cdot \frac{1}{2}C_4H_6O_3$ : C, 54.57%; H, 3.30%; N, 14.14%. Trouvé: C, 54.99%; H, 3.07%; N, 14.28%.

### 3,8-Dichloro-6-cétoquinazolo[1,2,2',3']indazol ( $k_1$ ) (III)

On chauffe à reflux 0.522 g de 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol et 1 g d'hydroxyde de potassium dans 20 ml de glycol. Durant l'ébullition il se dégage de l'ammoniac. La solution prend d'abord une teinte rouge et tourne rapidement au jaune-vert pâle. La réaction terminée, on refroidit la solution, la dilue par l'eau à environ 100 ml, l'acidifie à l'acide acétique ou chlorhydrique et l'abandonne à la température ambiante pendant 12 heures. On filtre ensuite le solide, le lave abondamment à l'eau et le sèche sous-vide. Le 3, 8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (0.434 g) cristallise dans la N,N-diméthylformamide et fournit 0.315 g d'aiguilles jaunes de point de fusion de 382° qui contiennent une demi-molécule de solvant de cristallisation. Calculé pour  $C_{14}H_7ON_3Cl_2 \cdot \frac{1}{2}HCON(CH_3)_2$ : C, 54.81%; H, 2.82%; N, 14.43%; Cl, 20.88%. Trouvé: C, 55.13%; H, 2.79%; N, 13.99%; Cl, 21.10%.

Lorsqu'on purifie le produit brut par sublimation, on obtient, sous 12 mm de mercure entre 250 et 350°, un sublimé jaune pâle fondant à 378–380°. Calculé pour  $C_{14}H_7ON_3Cl_2$ : C, 55.28%; H, 2.32%; O, 5.26%; N, 13.82%; Cl, 23.32%. Trouvé: C, 55.18%; H, 2.28%; O, 5.60%; N, 13.85%; Cl, 23.22%. Spectre infrarouge: 1670 ( $=CO$ ), 2400–3200  $cm^{-1}$  ( $=CO-NH-$  associé).

Le sel de potassium s'obtient lorsqu'on fait bouillir du 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (100 mg) dans la potasse à 10% (15 ml). Après une demi-heure d'ébullition, on ajoute prudemment la quantité d'eau chaude requise pour rendre la solution limpide et on la laisse refroidir à la température ambiante. Le sel cristallise en fines aiguilles de point de fusion de 420–422° avec deux molécules d'eau. Calculé pour  $C_{14}H_6ON_3Cl_2K \cdot 2H_2O$ : C, 44.57%; H, 2.67%; N, 11.14%; Cl, 18.80%. Trouvé: C, 43.92%; H, 2.51%; N, 10.71%; Cl, 18.95%. Dans l'isopropanol ou la N,N-diméthylformamide le sel de potassium cristallise en aiguilles jaune pâle de point de fusion 410°. Calculé pour  $C_{14}H_6ON_3Cl_2K \cdot H_2O$ : C, 46.67%; H, 2.24%; N, 11.66%. Trouvé: C, 46.89%; H, 2.53%; N, 11.47%.

Le sel de baryum s'obtient en additionnant de l'eau de baryte à une solution de sel de potassium. Le sel de baryum précipite. Il est filtré, lavé à l'eau et séché. Il noircit vers 340°, mais ne fond pas au-dessous de 500°. Calculé pour  $Ba(C_{14}H_6ON_3Cl_2)_2 \cdot 4H_2O$ : C, 41.22%; H, 2.47%; N, 10.30%. Trouvé: C, 40.91%; H, 2.30%; N, 10.03%.

### Ether méthylique du 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol

Le 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (50 mg) est bouilli à reflux pendant une demi-heure dans 50 ml de potasse à 10%. Le sel de potassium précipite à la température ambiante. Il est dissous par addition d'eau et, sous agitation, est traité par un excès de sulfate de méthyle (1 ml). Un solide jaune pâle précipite presque immédiatement. Après un séjour de 6 heures à la température ambiante, il est essoré, lavé, séché et cristallisé successivement dans l'acide acétique et le xylène. L'éther méthylique du 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol apparaît sous la forme d'aiguilles microscopiques de

point de fusion de 278–279°. Calculé pour  $C_{15}H_9ON_3Cl_2$ : C, 56.62%; H, 2.85%; N, 13.20%. Trouvé: C, 57.02%; H, 2.94%; N, 13.05%.

*5-Chloro-3-nitrosamino-2-[4-chloro-2-carboxyphényl-(2)]indazol (XII)*

Le 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol (0.140 g) est dissous dans l'acide sulfurique à 70% (en volume) et la solution, sous agitation, est refroidie à 5°. À la suspension du sulfate, on ajoute goutte à goutte, tout en maintenant la solution à 10°, 2 ml d'une solution de nitrite de sodium à 20%. On laisse séjourner le mélange dans le bain glacé durant 2 heures, on décompose ensuite l'excès de nitrite par addition d'urée et dilue finalement le tout par l'eau à 50 ml. On essore, lave et sèche le précipité (0.146 g). Cristallisé successivement dans la N,N-diméthylformamide et l'acide acétique, le 5-chloro-3-nitrosamino-2-[4-chloro-2-carboxyphényl-(2)]indazol forme des aiguilles jaunes de point de fusion de 418–420°. Calculé pour  $C_{14}H_8O_3N_4Cl_2$ : C, 47.88%; H, 2.30%; N, 15.96%. Trouvé: C, 48.18%; H, 1.97%; N, 15.81%. Spectre infrarouge: 1680  $cm^{-1}$  (—COOH).

*3,8-Dichloro-6-imino-11,12-dioxoquinazolo[1,2,2',3']indazol (X)*

On dissout 0.536 g de 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol dans 60 ml d'acide acétique glacial, et, tout en maintenant la température de la solution au-dessous de 20°, on ajoute 1.5 ml d'acide perchlorique à 60% et ensuite 1.5 ml de peroxyde d'hydrogène à 95%. On chauffe à reflux jusqu'à ce que soit disparue la coloration rouge qui apparaît au début de l'ébullition, ce qui exige environ une demi-heure. La solution est alors refroidie, diluée par l'eau à environ 175 ml et alcalinisée par la soude diluée. Le 3,8-dichloro-6-imino-11,12-dioxoquinazolo[1,2,2',3']indazol (0.134 g) jaune pâle précipite dès que le pH atteint la valeur de 3 à 4. Recristallisé deux fois dans le xylène, il se présente sous forme d'aiguilles crèmes de point de fusion de 252–254°. Calculé pour  $C_{14}H_8O_2N_4Cl_2$ : C, 50.14%; H, 2.40%; N, 16.72%. Trouvé: C, 50.16%; H, 2.45%; N, 16.44%.

*3,8-Dichloro-6-céto-11,12-dioxoquinazolo[1,2,2',3']indazol (XI)*

À une suspension de 0.310 g de 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol dans 75 ml d'acide acétique, on ajoute à la température ambiante 1.5 ml d'acide perchlorique et 1.5 ml de peroxyde d'hydrogène à 95%. Après 1½ heure d'ébullition à reflux, la solution est refroidie et diluée par l'eau. La solution colloïdale, qui apparaît d'abord, se coagule après quelque temps en un solide jaune (0.110 g). Celui-ci est essoré et sublimé entre 150 et 250° sous 12 mm de mercure. On recueille le 3,8-dichloro-6-céto-11,12-dioxoquinazolo[1,2,2',3']indazol qui fond à 250–252°, puis se solidifie et fond de nouveau à 266°. Calculé pour  $C_{14}H_8O_3N_4Cl_2$ : C, 49.87%; H, 2.39%; N, 12.46%. Trouvé: C, 49.97%; H, 2.42%; N, 12.29%.

*4,4'-Dichloro-2-carbamylazoxybenzène (XIII)*

En évaporant à siccité les filtrats provenant de la cristallisation du 3,8-dichloro-6-iminoquinazolo[1,2,2',3']indazol, la substance *k* décrite précédemment, et en cristallisant le résidu successivement dans divers solvants tels que l'acide acétique, l'éthanol et le 2-chloroéthanol, on parvient à isoler une troisième substance (*n*). Pour obtenir le 4,4'-dichloro-2-carbamylazoxybenzène à l'état pur, il faut le traiter à chaud par la soude alcoolique diluée, l'essorer, le laver à l'eau et le recristalliser dans l'acide acétique dans lequel il forme des aiguilles crèmes fondant à 228–229°. Calculé pour  $C_{13}H_9O_2Cl_2$ : C, 50.34%; H, 2.92%; N, 13.55%. Trouvé: C, 50.33%; H, 2.87%; N, 13.56%. Spectre ultraviolet: max  $\lambda_{\mu}$  335 ( $\epsilon$  20,800). Spectre infrarouge: 1680 (=CO), 3150 et 3400  $cm^{-1}$  (—CONH<sub>2</sub>).



*6-Iminoquinazolo[1,2,2',3']indazol (k') (IV)*

Le solide (A'), qui est obtenu à la suite de la réaction de von Richter avec le nitrobenzène (20 g) dans le glycol à 90% (200 ml) (1), cristallise dans l'éthanol en aiguilles (1.3 g) lustrées et transparentes de couleur jaune-verdâtre et de point de fusion de 222–223°. Toutefois, la plupart du temps, pour réussir à le purifier, il faut d'abord l'extraire à la butanone, évaporer l'extrait à siccité et cristalliser le résidu dans le même solvant. Calculé pour  $C_{14}H_{10}N_4$ : C, 71.77%; H, 4.30%; N, 23.92%. Trouvé: C, 71.72%; H, 4.41%; N, 23.78%. Spectre infrarouge: 1670 et 3310 ( $=NH$ ),  $3120\text{ cm}^{-1}$  ( $-NH-$ ). Spectre ultraviolet: max  $\lambda_{m\mu}$  236 ( $\epsilon$  56,800);  $\lambda_{m\mu}$  300 ( $\epsilon$  18,800);  $\lambda_{m\mu}$  375 ( $\epsilon$  9,500).

Le chlorhydrate du 6-iminoquinazolo[1,2,2',3']indazol s'obtient en dissolvant l'indazol IV dans l'acide chlorhydrique concentré à 60°. En laissant refroidir la solution à la température ambiante, le chlorhydrate cristallise. Il forme des cristaux jaunes de point de fusion de 279–280° (lit. 277° (2)).

Une solution de 2,2'-dicyanoazoxybenzène (1.0 g) et de cyanure de potassium (30.0 g) dans le glycol à 90% (100 ml) est bouillie à reflux pendant 3 heures, refroidie et diluée par l'eau (500 ml). Le précipité jaune-verdâtre (0.051 g), qui apparaît, est filtré, lavé, séché et extrait à la butanone. L'extrait est évaporé à siccité. Le résidu, cristallisé deux fois dans l'éthanol (noir animal), fournit des lamelles lustrées et transparentes de point de fusion de 221–222°. Un point de fusion mixte de cette substance et du 6-iminoquinazolo[1,2,2',3']indazol obtenu précédemment n'est pas abaissé et les spectres infrarouges des deux composés sont identiques.

*6-Cétoquinazolo[1,2,2',3']indazol (k<sub>1</sub>') (V)*

Le 6-iminoquinazolo[1,2,2',3']indazol (0.500 g) est traité par l'hydroxyde de potassium dans le glycol (10 ml), comme il est décrit précédemment pour le 3,8-dichloro-6-cétoquinazolo[1,2,2',3']indazol. Le produit obtenu fournit par sublimation, à environ 280° sous 12 mm de mercure, un sublimé de 6-cétoquinazolo[1,2,2',3']indazol. Il cristallise dans l'acide acétique en aiguilles jaunes de point de fusion de 334–336°. Calculé pour  $C_{14}H_9ON_3$ : C, 71.48%; H, 3.85%; N, 17.86%. Trouvé: C, 71.55%; H, 3.85%; N, 17.94%. Spectre infrarouge: 1680 ( $=CO$ ),  $2500\text{--}3200\text{ cm}^{-1}$  ( $=C-NH-$  associé).

## REMERCIEMENTS

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# THE KINETICS AND MECHANISM OF THE $\text{Cu}^{++}$ -CATALYZED REDUCTION OF $\text{Cr}^{\text{VI}}$ BY HYDROGEN IN AQUEOUS SOLUTIONS<sup>1</sup>

E. A. HAHN AND E. PETERS

## ABSTRACT

The kinetics of the  $\text{Cu}^{++}$ -catalyzed reduction of  $\text{Cr}^{\text{VI}}$  by  $\text{H}_2$  in aqueous perchlorate solutions have been investigated between 160° and 200° C. The mechanism proposed to account for the kinetics gives rise to a rate law of the form

$$\frac{-d[\text{H}_2]}{dt} = \frac{k_1[\text{Cu}^{++}][\text{H}_2]\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]\}}{[\text{H}^+] + (k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]},$$

where

$$k_1 = 5.3 \times 10^{10} \exp(-25,800/RT) \text{ liter mole}^{-1} \text{ sec}^{-1},$$

$$k_2/k_{-1} = 2.5 \pm 0.7 \quad \text{and} \quad (k_3/k_{-1}) = 48 \pm 10.$$

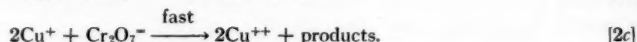
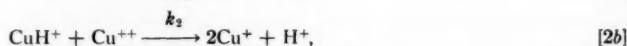
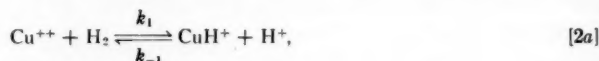
As a consequence of these studies an important anomaly between the previously published rate law for dichromate reduction and a more recent kinetic study of the cupric-perchlorate-catalyzed hydrogen-oxygen recombination has been resolved.

## INTRODUCTION

The reduction of dichromate by hydrogen in aqueous cupric perchlorate solutions has been described previously by Peters and Halpern (1), who observed simple second-order kinetics in the temperature range 80° to 140° C, the reaction being zero-order in dichromate, first-order in hydrogen, and first-order in cupric perchlorate. It was noted that perchloric acid additions above .025 *M* retarded the rate slightly, and subsequent studies (2) showed that this acid effect, at concentrations up to 1.00 *M*  $\text{HClO}_4$ , could be incorporated into the rate law to yield the expression

$$[1] \quad \frac{-3d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = \frac{-d[\text{H}_2]}{dt} = \frac{k_1[\text{H}_2][\text{Cu}^{++}]^2}{[\text{Cu}^{++}] + (k_{-1}/k_2)[\text{H}^+]},$$

where  $k_1$ ,  $k_{-1}$ , and  $k_2$  are rate constants applicable to the slow steps of the following reaction sequence:



The rate law predicts a simple second-order reaction at low  $\text{H}^+$  concentrations, as previously observed, and a more complex reaction approaching second-order dependence in copper at high acidities, which was later verified (2). Subsequently, it was observed that the initial reduction kinetics for copper precipitation from perchlorate solutions by hydrogen (3) followed the same law at temperatures up to 160° C. In this case a disproportionation process replaces step [2c] above, i.e.



The object of the present investigation was to determine the effect of higher temperatures on the dichromate reaction, which had not been studied above 140° C, in order

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Contribution from the Department of Mining and Metallurgy, University of British Columbia, Vancouver, British Columbia.

to learn more about the reaction mechanism and in particular the rate constants  $k_{-1}$  and  $k_2$ . Because of the very strong temperature effect, which doubled the reaction rate for approximately every 10° C increase in temperature, the cupric perchlorate concentrations were lowered substantially, while the initial dichromate levels were raised from those used in previous investigations in order to obtain reaction times long enough for good rate measurements.

#### EXPERIMENTAL

The experiments were conducted in the 1-gallon titanium-lined autoclave described in connection with earlier investigations (1, 2, 3, 4, 5), using a similar procedure. Silicon carbide, about 240 mesh, was packed between the titanium liner and the stainless steel autoclave to provide a heat transfer medium, to replace water which had been used previously, but which was unsatisfactory at higher temperatures. Glass wool was packed above the silicon carbide powder to prevent contamination of the solution. By this arrangement the temperature was controlled to within  $\pm 0.3^\circ\text{C}$  with a Leeds and Northrup Micromax controller-recorder.

The exit tube from the sampling valve consisted of 3 feet of titanium tubing in the form of a coil which was water-cooled to eliminate flashing of the samples when they were drawn from the autoclave at temperatures up to 200° C.

All chemicals used were of reagent grade, supplied by Baker and Adamson Limited. Stock solutions were prepared with distilled water. Cupric perchlorate was prepared from perchloric acid and cupric oxide. Commercial hydrogen gas, supplied in cylinders by Canadian Liquid Air Company, was used without further purification.

Two and one-half liters of solution of the desired composition were placed in the titanium liner of the autoclave, which was then sealed, flushed with nitrogen, and heated to the desired temperature. Experiments were performed at temperatures of 160°, 180°, and 200° C. Hydrogen was introduced after the autoclave had been maintained at the reaction temperature for an appreciable amount of time. Samples of the solution were withdrawn at intervals both before and after the addition of hydrogen, and analyzed to determine the course of the reaction. Dichromate determinations were made spectrophotometrically at the 350 m $\mu$  absorption peak, using a Beckman DU spectrophotometer. Copper was determined electrolytically, and free acid was titrated with sodium tetraborate solutions.

#### RESULTS AND DISCUSSION

Early in this investigation it was observed that the plots depicting the reduction of dichromate by hydrogen in the presence of cupric perchlorate were not straight lines, as found at lower temperatures, lower dichromate levels, and higher copper concentrations, by previous investigators (1, 2). Typical rate plots, shown in Fig. 1, indicate that the rate is dichromate dependent, and the extent of this dependence increases as the acidity is increased.

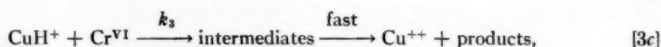
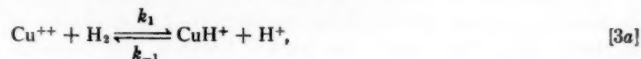
Rate measurements were made from these plots by measuring slopes at various dichromate levels.\*

On the assumption that the kinetics of this reaction obeyed a rate law that bears some

\*To make rate measurements, the best smooth curve was drawn through the points with a flexible curved ruler, and tangents were drawn by the mirror-image method. The measurements have a maximum precision near the mid-point of the curve of about  $\pm 5\%$ , with the precision falling off at both ends, because of the scatter of experimental points.

relation to equation 1, in spite of the partial dichromate dependence, the effect of varying the hydrogen ion concentration was studied. The reduction plots of one set of these experiments are presented in Fig. 1, and the inverse rates of these plots measured at several dichromate levels are shown in Fig. 2. The latter plots are seen to be straight lines, indicating that an inverse dependence of the rate on hydrogen ion concentration exists at all dichromate levels. In the same plot, the dichromate dependence appears to vanish at low hydrogen ion concentration.

A mechanism has been proposed that will account for all of these observations and involves a simple modification of mechanism [2]. The steps are:



When this mechanism is subjected to the steady-state treatment in  $\text{CuH}^+$ , the following rate law is obtained:

$$[4] \quad \frac{-3d[\text{Cr}_2\text{O}_7^{--}]}{dt} = \frac{-d[\text{H}_2]}{dt} = \frac{k_1[\text{Cu}^{++}][\text{H}_2]\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]\}}{[\text{H}^+] + (k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]}.$$

The above expression can be inverted to give the function in  $\text{H}^+$  that is plotted in Fig. 2. The intercept on this plot is seen to be

$$[5] \quad I = \frac{1}{k_1[\text{Cu}^{++}][\text{H}_2]},$$

while the slope can be expressed as

$$[6] \quad S = \frac{1}{k_1[\text{Cu}^{++}][\text{H}_2]\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]\}}.$$

From equation 6, it is apparent that the reciprocals of the slopes in Fig. 2 should be linear in  $\text{Cr}^{\text{VI}}$ . This is demonstrated in Fig. 3, where the inverse slopes of the lines in Fig. 2,  $1/S$ , are plotted against  $\text{Cr}^{\text{VI}}$  for the three different temperatures. The equation representing these lines is obtained by inverting equation 6, i.e.,

$$[7] \quad \frac{1}{S} = k_1[\text{Cu}^{++}][\text{H}_2]\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]\}.$$

Thus it can be seen that the slopes of Fig. 3 represent the value of  $k_1[\text{Cu}^{++}][\text{H}_2](k_3/k_{-1})$  and the intercepts represent the value  $k_1[\text{Cu}^{++}][\text{H}_2](k_2/k_{-1})[\text{Cu}^{++}]$ .

A further simplification can be obtained by dividing equation 7 through by  $k_1[\text{Cu}^{++}][\text{H}_2]$  which is the value of the reaction rate extrapolated to zero hydrogen ion concentration, that is, the inverse intercept of Fig. 2, expressed by equation 5. The resulting expression is given by

$$[8] \quad \frac{I}{S} = \frac{k_2}{k_{-1}}[\text{Cu}^{++}] + \frac{k_3}{k_{-1}}[\text{Cr}^{\text{VI}}].$$

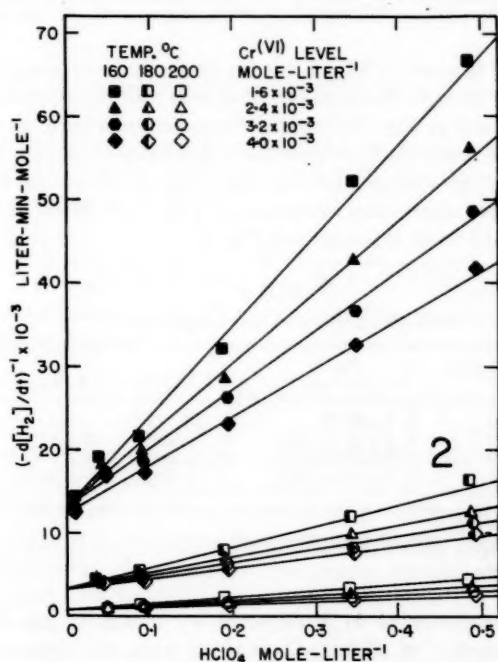
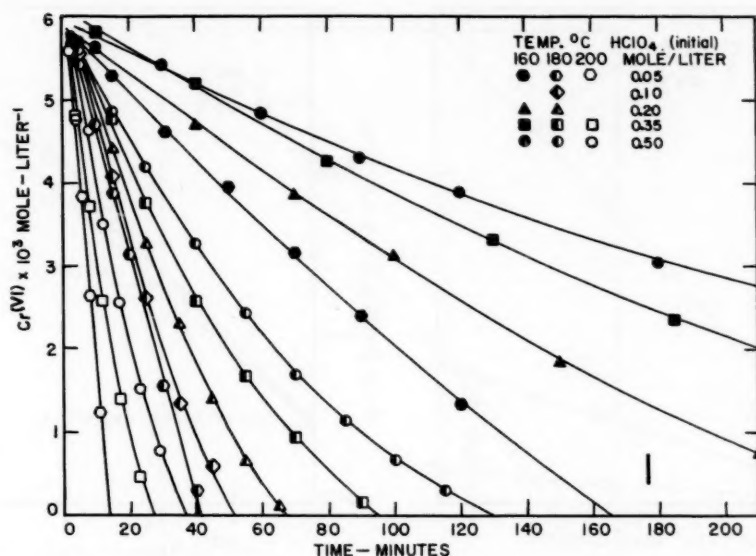
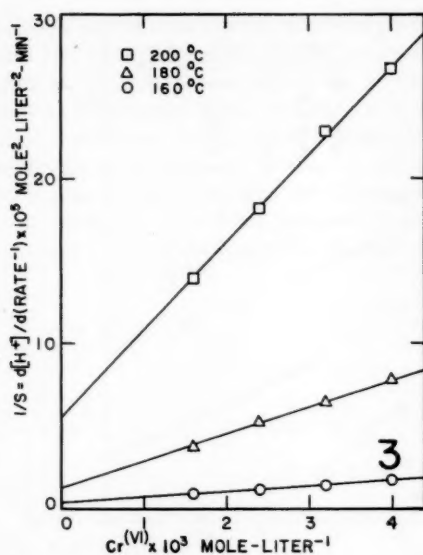
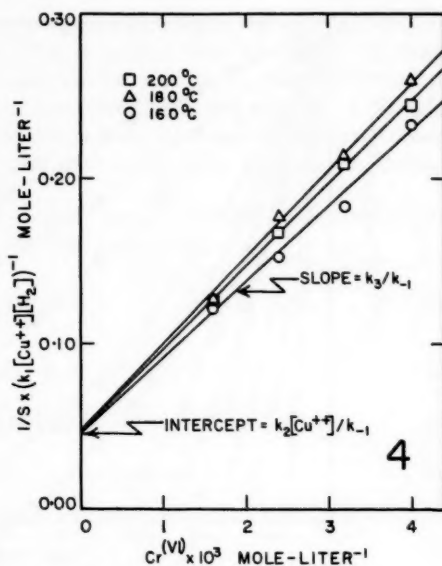

 FIG. 1. Typical rate plots of the dichromate reduction by hydrogen: 10 atm  $\text{H}_2$ , 0.02 M  $\text{Cu}(\text{ClO}_4)_2$ .

 FIG. 2. Dependence of  $1/\text{rate}$  on  $\text{H}^+$  concentration: 10 atm  $\text{H}_2$ , 0.02 M  $\text{Cu}(\text{ClO}_4)_2$ .



FIG. 3. Dependence of the function  $d[H^+]/d(\text{rate}^{-1})$  on the dichromate level in solution.FIG. 4. Dependence of the function  $(d[H^+])/ \{k_1[Cu^{++}][H_2] \times d(\text{rate}^{-1})\}$  on the dichromate level.

A plot of  $I/S$  vs.  $Cr^{VI}$  is given in Fig. 4, for the three temperatures that were studied. It can be seen that fairly straight lines are obtained and that the temperature dependence that appears so pronounced in Fig. 3 virtually disappears in Fig. 4. It can, therefore, be concluded that only  $k_1$  is particularly temperature dependent and that  $k_2/k_{-1}$  and  $k_3/k_{-1}$  are relatively insensitive to temperatures in this region. Values of  $k_2/k_{-1}$  and  $k_3/k_{-1}$  that are obtained from the slopes and intercepts of Fig. 4 are listed in Table I, together with values of  $k_1$  obtained from intercepts of Fig. 2.

TABLE I  
Rate constants at various temperatures

Temperature, °C	$k_1$ , l. mole <sup>-1</sup> sec <sup>-1</sup>	$k_2/k_{-1}$	$k_3/k_{-1}$
110	$9.5 \times 10^{-3} \dagger$	3.85 $\ddagger$	—
160	$5.4 \times 10^{-3} \pm 15\%$	$2.7 \pm 30\%$	$42 \pm 20\%$
180	$1.8 \times 10^{-2} \pm 15\%$	$2.3 \pm 30\%$	$54 \pm 20\%$
200	$5.7 \times 10^{-2} \pm 15\%$	$2.6 \pm 30\%$	$49 \pm 20\%$

\*Obtained from intercepts in Fig. 2, using  $Cu^{++} = .02$  mole/liter and new  $H_2$  solubility data (6).

†Values at 110° C were obtained from reference 2.

‡Value of  $k_2/k_{-1}$  at 110° C is the reciprocal of the value for  $k_{-1}/k_2$  ( $= 0.26$ ) given in reference 2.

The temperature dependence of  $k_1$  is depicted by means of an Arrhenius plot in Fig. 5. The activation energy of 25.8 kcal, obtained from the slope of this plot, is in excellent agreement with the value (26.6 kcal), obtained earlier (5). The rate-constant  $k_1$  is thus given by

$$[9] \quad k_1 = 5.3 \times 10^{10} \exp(-25,800/RT) \text{ liter mole}^{-1} \text{ sec}^{-1}.$$

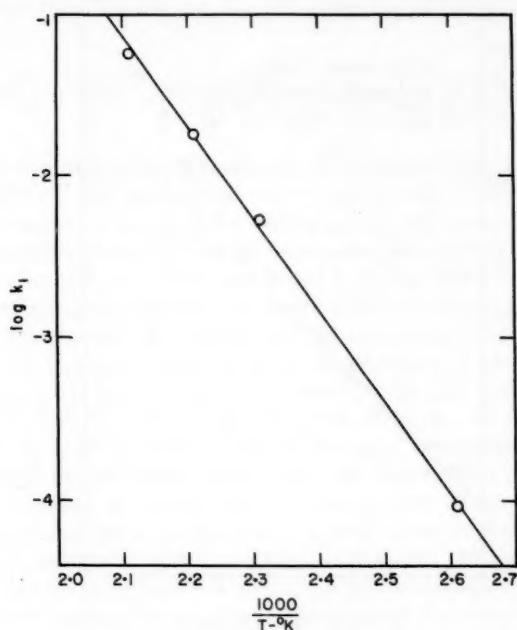


FIG. 5. Arrhenius plot of  $k_1$ : 0.02 M  $\text{Cu}(\text{ClO}_4)_2$ , 10 atm  $\text{H}_2$ .

The plots shown in Figs. 1-4 inclusive indicate that the data are consistent with the proposed mechanism [3], and the resulting rate law [4]. The data can be treated another way, by inverting equation 4 to obtain

$$[10] \quad \frac{1}{R} = \frac{[\text{H}^+]}{R_0\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3/k_{-1})[\text{Cr}^{\text{VI}}]\}} + \frac{1}{R_0}$$

where  $R$  is the measured rate  $= (-d[\text{H}_2])/dt$  and  $R_0$  is the value of  $k_1[\text{Cu}^{++}][\text{H}_2]$ . Rearranging the above we obtain

$$[11] \quad \frac{R[\text{H}^+]}{R_0 - R} = \frac{k_2}{k_{-1}}[\text{Cu}^{++}] + \frac{k_3}{k_{-1}}[\text{Cr}^{\text{VI}}]$$

and a linear plot would be expected if the function  $(R[\text{H}^+])/(R_0 - R)$  were plotted against  $\text{Cr}^{\text{VI}}$ . The results of this type of a plot, using three of the 180° C experiments, are depicted in Fig. 6. There is a significant departure from linearity in both directions at higher  $\text{Cr}^{\text{VI}}$  levels. However, the rate measurements in this region are erratic because they are near the beginning of a run. The best results are obtained on this form of plot when using the highest acid experiments, since in this case the rate difference,  $R_0 - R$ , is the largest value obtainable.

The significance of this reaction is that a process that is first-order in  $\text{Cr}^{\text{VI}}$  is competing with a forward reaction involving  $\text{Cu}^{++}$  and a back reaction involving  $\text{H}^+$ . The effects of these three species are interrelated through the three terms in the denominator of equation 4, and the dependence of the forward reaction on  $[\text{H}^+]$ ,  $[\text{Cu}^{++}]$ , or  $[\text{Cr}^{\text{VI}}]$  is a function of the relative values of these three terms. At low values of  $[\text{H}^+]$  the equation

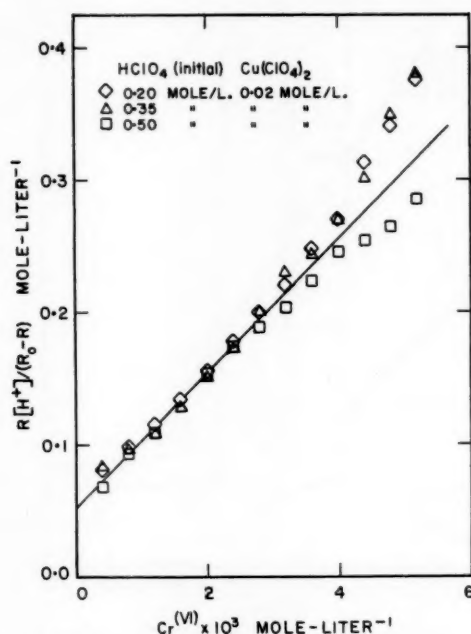
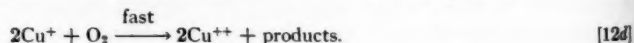
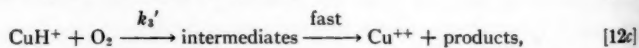
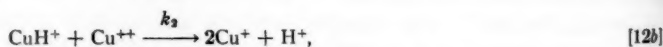
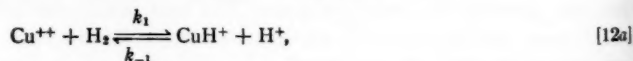


FIG. 6. Dependence of the function  $(\text{rate} \times [\text{H}^+]) / (k_1[\text{Cu}^{++}][\text{H}_2] - \text{rate})^{-1}$  on the dichromate level: 180° C.

reduces to a second-order reaction that is first-order in each of  $\text{Cu}^{++}$  and  $\text{H}_2$ . At high  $\text{H}^+$  concentrations the reaction may be second-order in  $\text{Cu}^{++}$  and zero-order in  $\text{Cr}^{\text{VI}}$ , or first order in each of  $\text{Cu}^{++}$  and  $\text{Cr}^{\text{VI}}$ , depending on their relative concentrations.

Of interest here is a related reaction involving the recombination of hydrogen and oxygen in nuclear reactors, which is catalyzed by  $\text{Cu}^{++}$  ions. This reaction was studied in sulphate and in perchlorate solutions at temperatures in the 200° to 300° C range by McDuffie and co-workers (7). McDuffie found that at 250° C and in solutions containing up to .05 mole/liter free perchloric acid, the reaction was first-order in  $\text{Cu}^{++}$  and independent of acidity. He observed that this was inconsistent with the rate law expressed by equation 1 unless the value for  $k_{-1}/k_2$  was far smaller than 0.26 as predicted by Peters and Halpern (1), because the value of  $[\text{Cu}^{++}]$  in McDuffie's work was very small, of the order of 0.002 mole/liter.

However, if oxygen, like  $\text{Cr}^{\text{VI}}$ , directly attacks the  $\text{CuH}^+$  complex, the rate expression describing the oxygen-hydrogen recombination kinetics would resemble equation 4, with  $\text{O}_2$  replacing  $\text{Cr}^{\text{VI}}$ . This mechanism would be written as follows:



The rate expression for this mechanism, obtained via the steady-state approximation in  $\text{CuH}^+$ , is

$$[13] \quad \frac{-2d[\text{O}_2]}{dt} = \frac{-d[\text{H}_2]}{dt} = \frac{k_1[\text{Cu}^{++}][\text{H}_2]\{(k_2/k_{-1})[\text{Cu}^{++}] + (k_3'/k_{-1})[\text{O}_2]\}}{[\text{H}^+] + (k_2/k_{-1})[\text{Cu}^{++}] + (k_3'/k_{-1})[\text{O}_2]}.$$

The conditions under which McDuffie *et al.* examined the kinetics in perchlorate solutions were  $250^\circ\text{C}$ , .002 mole/liter  $\text{Cu}^{++}$ , up to .05 mole/liter  $\text{H}^+$ , and initial oxygen partial pressures of the order of 400 p.s.i. At this pressure, the application of known oxygen solubility data (8) yields a concentration of .076 mole/liter  $\text{O}_2$ .

Assuming the value of  $k_2/k_{-1}$  to be unchanged from the  $200^\circ\text{C}$  value of 2.6 the second term of the denominator of equation 13,  $(k_2/k_{-1})[\text{Cu}^{++}]$ , would have a value of .0052. The first denominator term  $[\text{H}^+]$  would be .05 and, since McDuffie did not observe an acid dependence, this term must be small compared with the third term,  $(k_3'/k_{-1})[\text{O}_2]$ . This last term must have a value of at least 0.5 for the acid effect to be less than 10%. At .076 mole/liter  $\text{O}_2$ , this places the value of  $k_3'/k_{-1}$  at greater than 6.6. Such a large value is entirely reasonable in view of the large values of  $k_3/k_{-1}$  observed in the  $160^\circ$  to  $200^\circ\text{C}$  range in the present work when the oxidant is  $\text{Cr}^{\text{VI}}$  instead of  $\text{O}_2$ , even though there is no reason to assume that  $k_3'$  and  $k_3$  must be equal.

A relatively surprising result of this study is that there is no significant temperature dependence of the rate constant ratios  $k_2/k_{-1}$  and  $k_3/k_{-1}$ . These ratios have not been determined with sufficient precision for accurate analysis, but it is clear that the activation energies of the three competing reactions involving the decomposition of  $\text{CuH}^+$  do not differ by more than about 1.5 kcal/mole. This is not sufficient to account for the relatively large value of the rate constant ratio  $k_3/k_{-1}$ , which at a value of 48 would require an activation energy difference of 3.4 kcal in favor of the  $\text{Cr}^{\text{VI}}$  reaction, although it can account for the value of  $k_2/k_{-1}$ , which at 2.6 would require an activation energy difference of only 800 calories. It is therefore likely that activation entropy differences must be called upon to account completely for the differences in the rates by which  $\text{CuH}^+$  is attacked by different oxidants.

### CONCLUSIONS

The kinetics of dichromate reduction by hydrogen in aqueous cupric perchlorate solutions are more complex than previously noted (2) in that they show some dichromate dependence at low  $\text{Cu}^{++}$  and high  $\text{Cr}^{\text{VI}}$  levels. A mechanism involving the direct attack of the  $\text{CuH}^+$  intermediate by both  $\text{Cu}^{++}$  and  $\text{Cr}^{\text{VI}}$ , followed by fast conversion of resulting intermediates to the stable final species, has been shown to be consistent with these results. The same form of attack of  $\text{CuH}^+$  by  $\text{O}_2$  in the hydrogen - oxygen recombination studies by McDuffie *et al.* (7) could account for the kinetics obtained by these workers who observed no acid dependence at  $250^\circ\text{C}$  in the cupric perchlorate system, such as would be expected if mechanism [2] is applied, where  $\text{CuH}^+$  is attacked only by  $\text{H}^+$  and  $\text{Cu}^{++}$ .

### ACKNOWLEDGMENTS

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# THE INFRARED AND THE NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF POLYPHENYL DERIVATIVES OF THE ELEMENTS OF GROUPS IVb AND Vb<sup>1</sup>

C. N. R. RAO,<sup>2</sup> J. RAMACHANDRAN,<sup>3</sup> AND A. BALASUBRAMANIAN

## ABSTRACT

The near-ultraviolet absorption spectra of polyphenyl derivatives of the IVb and Vb elements have been studied in detail. In the case of the triphenyl derivatives of the Vb elements, the unshared *p*-electrons on the central atoms interact strongly with the  $\pi$ -orbitals of the benzene rings. When the central atoms do not possess unshared electrons as in the case of the derivatives of the IVb and the pentavalent Vb elements, there appears to be no such resonance interaction. The Hammett reactivity constants of the para- and meta-trityl, triphenylsilyl, and triphenylgermanyl groups are estimated to be close to zero. However, the reactivity constant of the triphenylsilyl group in the para position of phenol is estimated to be about 0.30. The infrared spectra of the phenyl derivatives of the IVb and Vb elements show smooth trends due to mass effects of the central atoms, in the C=C skeletal, C—H out-of-plane, and other vibrations. The absorption frequencies which are assigned to the phosphorus-phenyl and silicon-phenyl bonds in the literature do not appear to be unique for these linkages.

## INTRODUCTION

The preliminary results on the infrared and the near-ultraviolet absorption spectra of some polyphenyl derivatives of the IVb and Vb elements have been published earlier by Rao *et al.* (1). In this communication, the spectroscopy of these systems has been reported and discussed in detail. In the case of the Vb elements, the spectra of derivatives in which the central atoms possess and do not possess unshared *p*-electrons (i.e. derivatives of the atoms in their "trivalent" and "pentavalent" states respectively) have been studied. The ultraviolet and the infrared spectra of substituted tetraphenylmethane, tetraphenylsilicane, and tetraphenylgermanium have also been investigated in order to be able to estimate the reactivity and resonance parameters of these groups.

## EXPERIMENTAL

All the polyphenyl derivatives of the IVb and Vb elements (mentioned in Table I) were commercially available and they were further purified before use. The trityl, triphenylsilyl, and triphenylgermanyl benzene derivatives with functional groups were prepared by the methods reported by Benkeser *et al.* (2, 3, 4).

The ultraviolet absorption spectra were recorded using a Cary Model 11 recording spectrophotometer and a Hilger spectrophotometer, H700. All the solvents were fractionated before use.

The infrared spectra were recorded using a Baird-Atomic spectrometer (Model KM 1) and a Perkin-Elmer (Model 21) spectrometer, both with NaCl optics. The samples were prepared as mulls in Nujol or as solutions in chloroform. The relative intensities of the peaks have been recorded as follows: S, strong; M, medium; and W, weak. The carbonyl frequencies reported in Table III are correct to within 5 cm<sup>-1</sup>.

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## RESULTS AND DISCUSSION

All the triphenyl derivatives of the Vb elements show fairly strong bands in their ultraviolet spectra (Table I). Triphenylamine exhibits two bands at 228 and 297 m $\mu$ . By analogy with the assignments in aniline,\* the lower wavelength band is probably the

TABLE I

The near-ultraviolet absorption spectra of polyphenyl derivatives of elements of groups IVb and Vb\*

Compound	$\lambda_{\max}$ , m $\mu$	Compound	$\lambda_{\max}$ , m $\mu$	log $\epsilon_{\max}$	Compound	$\lambda_{\max}$ , m $\mu$
CH(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	250, 256, 263, 270	N(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	228, 297	3.87, 4.41	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Br	257†, 263, 269, 277
C(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	253†, 262, 272	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	260	4.06	As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Cl	256†, 260, 266, 273
Si(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	254, 260, 265, 271	As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	248	4.12	Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Br	252, 258, 263, 270
Sn(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	251, 258, 264, 269	Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	255	4.09	Sb(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Cl <sub>2</sub>	253, 258, 263, 270
Pb(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	250, 257, 263, 268†	Bi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	253†, 281.5	3.63	Bi(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Cl <sub>2</sub>	— — — —

\*All the spectra in 95% ethanol. †Shoulder.

so-called "primary" benzenoid band or the *E*-band. The longer wavelength band at 297 m $\mu$  is the "secondary" band or the *B*-band. The other triphenyl derivatives of the Vb elements (with the exception of triphenylbismuthine) show only one band in the near-ultraviolet region, which may be tentatively assigned to the *B*-band.†

The *B*-band of benzene ( $\pi \rightarrow \pi^*$  transition around 260 m $\mu$ ) shows vibrational fine structure. The absence of the vibrational structure in the *B*-bands of the triphenyl derivatives of the Vb elements is probably due to the interaction of the non-bonded *p*-electrons on the central atoms with the  $\pi$ -orbitals of the benzene rings. Of course, one would imagine that the electrons are delocalized over the entire molecule (6). Further, there is a progressive increase in the *B*-band wavelength with the increase in the number of phenyl groups around the central atom. The *B*-bands of aniline, diphenylamine, and triphenylamine are found at 280, 285, and 297 m $\mu$  respectively. The phosphorus, arsenic, and antimony derivatives also show similar variations of the *B*-band. As Robertson and Matsen (5) have pointed out, the dissimilarity between the spectra of compounds (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>X and (C<sub>6</sub>H<sub>5</sub>)XH is a measure of the resonance interaction of the phenyl groups and the central atom. In general, the results of the present investigation and the interpretations offered are in agreement with the earlier work (6, 7, 8).

Among the triphenyl derivatives of the Vb elements, triphenylamine exhibits the *B*-band at the largest wavelength with the maximum intensity. This is understandable since nitrogen, being a first row element, will have greater tendency for double-bond formation. There is a marked decrease in the *B*-band wavelength and intensity, in the case of triphenylphosphine and a further decrease in triphenylarsine. In phosphorus, the 3*d*-shell is vacant, while in arsenic it is completely filled. While going from triphenylarsine to triphenylstibine and triphenylbismuthine, there is a progressive increase in the *B*-band wavelength (248, 256, and 280 m $\mu$  respectively). This is possibly due to the predominating influence of the decreasing ionization potential (9) of the central atom. Apparently, the similarity of the electronic structures of the inner shells in arsenic, antimony, and bismuth (all the three with filled *d*-shells) is responsible for exhibiting such a marked effect of the decreasing ionization potential on the absorption spectra. The importance of the

\*Aniline exhibits bands at 230 and 280 m $\mu$ . These have been labelled as "primary" and "secondary" bands by Doub and Vandenberg (J. Am. Chem. Soc. 69, 2714 (1947)); as *E* and *B* bands by Gillam and Stern (In Electronic absorption spectroscopy. Edward Arnold Ltd., London. 1957. p. 140).

†Jaffe (6) makes a similar assignment. The discussion of the results will not be affected by any possible change in the assignment.

ionization potentials in determining bathochromic shifts has been pointed out earlier (10, 11). Triphenylbismuthine exhibits another band at  $250\text{ m}\mu$  which may represent the dissociation process.

The polyphenyl derivatives of the  $Vb$  elements in their pentavalent state, in contrast to the triphenyl derivatives, show vibrational structure in their  $B$ -bands (Table I) similar to benzene itself. In Fig. 1, the spectra of triphenylstibine and triphenylstibonium-

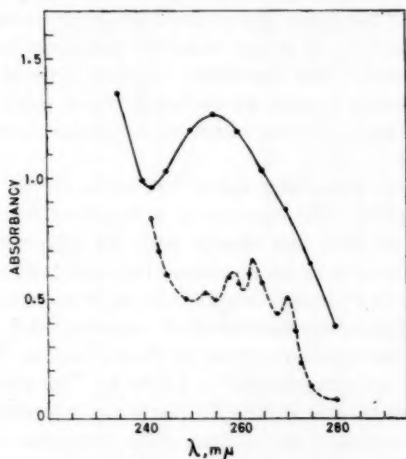


FIG. 1. Near-ultraviolet absorption spectra of triphenylstibine (—) and triphenylstiboniumdichloride (— —) in ethanol.

dichloride are reproduced for purposes of comparison. The presence of the vibrational structure in the  $B$ -bands of these derivatives of  $Vb$  elements indicate negligible or no resonance interaction of the central atoms with the  $\pi$ -orbitals of the benzene rings. This is understandable since the central atoms do not possess any unshared electrons. Further,  $B$ -band positions of these derivatives show little variation with the number of phenyl groups attached to the central atom, and the intensity seems to be directly proportional to the number of phenyl groups. The results with these derivatives agree well with the earlier work on similar systems (7, 8, 12) and the explanations offered are similar to those of Jaffe (6).

The ultraviolet spectra of the polyphenyl derivatives of the  $IVb$  elements (Table I) are very similar to the spectra of the derivatives of the  $Vb$  elements in their pentavalent state. Here also, the  $B$ -bands show vibrational structure. The  $B$ -band position does not depend on the number of phenyl groups and the intensity contribution by a phenyl group is constant and additive. The results on the  $IVb$  derivatives reported here are similar to those of Milazzo (13) and Bowden and Braude (7) on derivatives of the type  $C_6H_5MR_3$  ( $R$  = alkyl group).

Among the  $IVb$  derivatives, the silicon derivative seems to show a slightly larger bathochromic shift. Similarly, the phosphorus derivative seems to show a larger bathochromic shift among the  $Vb$  pentavalent derivatives. These observations may possibly be taken as evidence for the "expansion of the valence shells" in these two second row elements. The formation of  $\pi$ -bonds by the second row elements, using  $3d$  orbitals

appears to be quite general (14). Recently, reviews giving experimental evidence for  $d\pi$ -orbitals in silicon (15) and phosphorus (16) have been published. The inductive effects of phosphorus and silicon will also be considerably different from those of the corresponding first row elements. But, it is more likely that resonance or  $\pi$ -orbital interaction is responsible for the bathochromic shifts in these phosphorus and silicon derivatives rather than inductive effects.

The ultraviolet spectrum of pentaphenylphosphorus is supposed to be very close to that of triphenylphosphine.\* However, the ultraviolet spectrum of pentaphenylantimony shows vibrational fine structure. It is not possible, therefore, to explain Van Wazer's observation in a simple fashion. The possibility of some type of steric crowding in the case of pentaphenylphosphorus cannot be excluded. Such steric crowding will be less significant in the antimony derivative by virtue of the larger atomic volume of antimony compared with phosphorus.

The solvent effects on the ultraviolet spectra of some of the derivatives of the IVb and Vb elements were studied. The spectra of tetraphenylmethane and tetraphenylphosphoniumbromide did not show any change with the solvents. The triphenyl derivatives of the Vb elements showed very small solvent blue-shifts in polar solvents, although there is no possibility of  $n \rightarrow \pi^*$  transitions (17) in these molecules.

All the ortho-, meta-, and para-substituted trityl, triphenylsilyl, and triphenylgermanyl benzene derivatives show vibrational structure in their B-bands. The absorption maxima of some of the derivatives are summarized in Table II. The para-carbonyl derivatives show fairly well-defined peaks due to the E-bands (at wavelengths lower than their B-bands), while the meta-carbonyl derivatives show only the vibrational structure of the B-bands (see Fig. 2). The E-band wavelengths in the para-carbonyl derivatives vary in the order, trityl > triphenylsilyl > triphenylgermanyl. These differences are, however, very small in magnitude. In any case, it appears fairly certain that all the

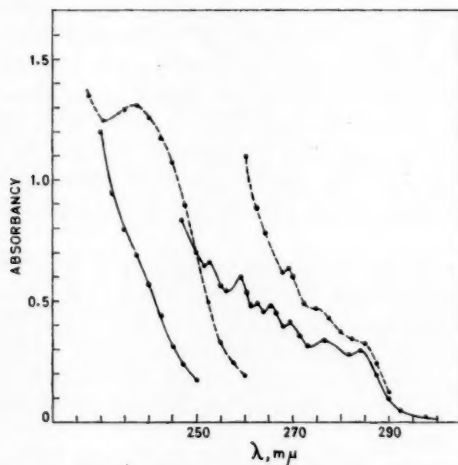


FIG. 2. Near-ultraviolet absorption spectra of *para*-triphenylgermanyl (---) and *meta*-triphenylgermanyl (—) benzoic acids.

\*J. R. Van Wazer. Personal communication.

TABLE II  
The near-ultraviolet absorption spectra of some *para*- and *meta*-substituted trityl-, triphenylsilyl-, and triphenylgermanyl-benzenes\*

Trityl			Triphenylsilyl			Triphenylgermanyl		
R	$\lambda_{\max}$ , m $\mu$		R	$\lambda_{\max}$ , m $\mu$		R	$\lambda_{\max}$ , m $\mu$	
<i>p</i> -OH	265, 274, 281, 287		<i>p</i> -OH	237, † 260, 265, 275, 283		—	—	—
<i>m</i> -OH	265, 274, 280, 285		<i>m</i> -OH	260, 265, 272, 285		—	—	—
<i>p</i> -COOMe	250 (266, 272, 284)†		<i>p</i> -CONH <sub>2</sub>	240 (261, 272)†		<i>p</i> -CONH <sub>2</sub>	238 (261, 274, 284)†	
<i>m</i> -COOMe	264, 272, 281, 285		<i>m</i> -CONH <sub>2</sub>	254, 260, 265, 272, 280†		—	—	—
<i>p</i> -COOH	243 (266, 272, 284)†		<i>p</i> -COOH	240 (260, 272)†		<i>p</i> -COOH	238 (264, 269, 276, 284)†	
<i>m</i> -COOH	263, 272, 280, 285‡		<i>m</i> -COOH	254, 262, 265, 272, 285‡		<i>m</i> -COOH	252, 258, 265, 276, 284‡	

\*All the spectra in 95% ethanol.

†Not very well defined.

‡All the maxima in the vibrational fine structure are not included.



three groups do not interact strongly with the benzene nucleus in these derivatives. The resonance parameters,  $\sigma_R$  (18), for the three groups in these systems are estimated to be less than 0.10 by employing the  $\lambda_{\max}$ - $\sigma_R$  correlations of Rao (19, 20). This is in agreement with the Hammett reactivity constants,  $\sigma$ , proposed for the meta- and para-trityl (3), triphenylsilyl, and triphenylgermany (4) groups by Benkeser *et al.*

Benkeser *et al.* (4) have pointed out that silicon and germanium atoms are capable of valence shell expansion when conjugated with strong electron-donating groups like in phenols and anilines. The *B*-bands of *m*- and *p*-trityl phenols are similar to those of *m*- and *p*-triphenylsilyl phenols (Table II). However, in *p*-triphenylsilylphenol an additional band is observed at 237  $m\mu$  which may be the displaced *E*-band. The *E*-band of phenol itself is found to be at about 210  $m\mu$ . The bathochromic shift observed in the *E*-band of *p*-triphenylsilylphenol may then be interpreted as due to the resonance interaction of the *p*-triphenylsilyl group (20). If the assignment of the 237  $m\mu$  band as the *E*-band is correct, the Hammett  $\sigma$ -value of the *p*-triphenylsilyl group may be estimated employing the correlation of the *E*-band absorption maxima with the  $\sigma$ -constants of substituents proposed by Rao (20). The Hammett  $\sigma$ -value\* thus estimated is about  $0.30 \pm 0.10$ . This is in agreement with the  $\sigma^-$ -value of 0.31 proposed by Benkeser *et al.* (4).

The carbonyl stretching frequencies in some of the meta- and para-trityl, triphenylsilyl, and triphenylgermany derivatives are shown in Table III. It is seen that the carbonyl

TABLE III  
Infrared carbonyl stretching frequencies in some *p*- and *m*-substituted  
trityl-, triphenylsilyl-, and triphenylgermany-benzenes\*

Substituents	$\nu_{C=O}$ , $cm^{-1}$	Substituents	$\nu_{C=O}$ , $cm^{-1}$
C(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>p</i> -COOCH <sub>3</sub>	1724	Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>p</i> -COOH	1704
C(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>m</i> -COOCH <sub>3</sub>	1723	Si(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>m</i> -COOH	1702
H, COOCH <sub>3</sub>	1723	Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>p</i> -COOH	1703
C(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>p</i> -COOH	1702	Ge(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>m</i> -COOH	1701
C(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> , <i>m</i> -COOH	1703	H, COOH	1704

\*In chloroform solution.

stretching frequencies in these compounds do not vary considerably from those in the unsubstituted compounds. It has been shown (21, 22) that the carbonyl frequencies in *m*- and *p*-substituted benzene derivatives may be directly correlated with the reactivity constants of the substituents. The data in Table III therefore suggest that the Hammett  $\sigma$ -values for the meta- and para-trityl, triphenylsilyl, and triphenylgermany groups are close to zero. This is in agreement with the conclusions drawn earlier from the ultraviolet absorption spectra and the kinetic data of Benkeser *et al.* (3, 4).

The major frequencies in the infrared spectra of the polyphenyl derivatives of IVb and Vb elements are summarized in Table IV. The C=C skeletal vibration around 1580  $cm^{-1}$ , some of the C—H in-plane deformation vibrations and ring vibrations, and the C—H out-of-plane deformation vibration around 740  $cm^{-1}$  show nice trends due to mass effects of the central atoms. Similar mass effects have been observed in the spectra of metal alkyls (23). Typical plots of the change in frequency,  $\Delta\nu$  (compared with the

\*This should be denoted by the symbol,  $\sigma^-$ , according to the recently accepted symbols for substituent constants, since this value of the parameter is only for phenols.



first compound of the series) against the atomic weight,  $A_M$ , of the central atom are shown in Fig. 3. The mass effects seem to be more prominent in the derivatives of the

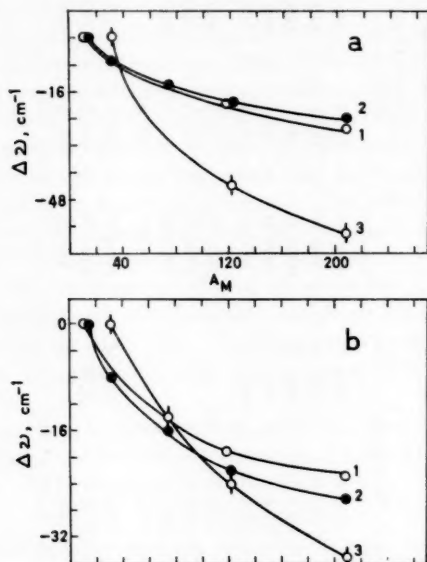


FIG. 3. Plots of  $\Delta \nu$  versus the atomic weight of the central atom in (1) tetraphenyl derivatives of IVb elements, (2) triphenyl derivatives of Vb elements, (3) polyphenyl derivatives of Vb elements in penta-valent state. (a) C=C skeletal vibration ( $1536\text{--}1594\text{ cm}^{-1}$ ) and (b) C—H out-of-plane deformation ( $726\text{--}764\text{ cm}^{-1}$ ).

Vb elements in their pentavalent state than in their trivalent state. Apparently, the resonance interaction involving the unshared electrons in the triphenyl derivatives is responsible for such a behavior.

The splitting reported earlier (1) in the C—H out-of-plane vibrations have been found to be mere solid state anomalies, since the splittings are not noticed in solution spectra. Daasch and Smith (24) have observed bands of moderate intensity in the regions  $1450\text{--}1435\text{ cm}^{-1}$  and  $1005\text{--}995\text{ cm}^{-1}$ , in compounds containing the phosphorus-phenyl linkages. Although the latter band has been suspected to arise from some activated ring vibration, the former band around  $1440\text{ cm}^{-1}$  was suggested to be characteristic of the phosphorus-phenyl linkage (25). On the basis of literature data, Bellamy (25) has suggested that bands around  $1429$  and  $1130\text{--}1090\text{ cm}^{-1}$  are characteristic of the silicon-phenyl linkage. A survey of the data in Table IV shows that bands are observed in all the above-mentioned regions in the spectra of several polyphenyl derivatives. It is therefore suggested that they may all be due to some activated ring vibrations. In the case of triphenylamine, however, definite assignment of the C—N linkage to the strong band at  $1337\text{ cm}^{-1}$  is possible.

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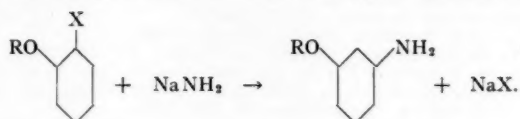
# HYDROGEN ISOTOPE EFFECT IN THE AMINATION OF CHLOROBENZENE BY SODAMIDE<sup>1</sup>

G. E. DUNN, PETER J. KRUEGER,<sup>2</sup> AND WALTER RODEWALD

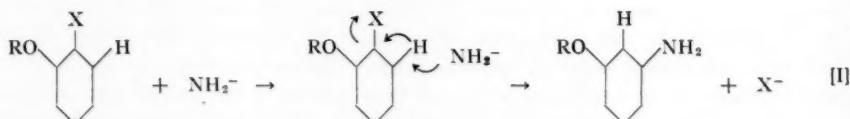
## ABSTRACT

Mixtures of chlorobenzene and chlorobenzene-2-<sup>3</sup>H have been subjected to partial amination by sodamide in liquid ammonia and both the unreacted starting material and the product aniline have been analyzed for deuterium. Deuterium in the aniline is distributed approximately equally between the ortho and meta positions. The results give strong support to the mechanism proposed by Roberts and co-workers in which the slow step is the formation of an intermediate, such as benzyne, which is symmetrical with respect to carbon atoms 1 and 2.

The amination of aromatic halides by alkali metal amides in liquid ammonia was discovered in 1936 by Bergstrom and co-workers (1), who were able to convert chloro-, bromo-, and iodo-benzene into aniline and a mixture of by-products containing diphenylamine, triphenylamine, and *p*-aminobiphenyl. Fluorobenzene did not react. In 1945 Gilman and Avakian reported that a number of ortho-halogenated ethers on treatment by Bergstrom's procedure gave meta-aminoethers (2) as illustrated by the equation



Bunnett and Zahler reviewed the reaction in 1951 (3) by which time aminations with rearrangement under the Bergstrom conditions had been observed with halogen substituents located ortho and para to ether, sulphide, sulphone, and trifluoromethyl groups. It had also been demonstrated, largely by Benkeser and co-workers (4), that the entering amide displaces a hydrogen atom ortho to the halogen atom. Bunnett and Zahler proposed a mechanism for the rearrangement in which attack by amide ion on carbon atom 2 of a halobenzene forces the migration of a hydride ion from carbon 2 to carbon 1 and the displacement of a halide ion by this hydride ion. The sequence of reactions in equation I below illustrates this mechanism.



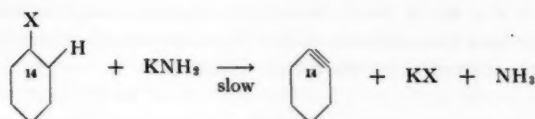
In 1953 Roberts and co-workers (5) showed that rearrangement occurs even in unsubstituted halobenzenes by demonstrating that chlorobenzene-1-<sup>14</sup>C with potassium amide in liquid ammonia gives aniline-1-<sup>14</sup>C and aniline-2-<sup>14</sup>C in almost equal amounts. The near equality of rearranged and unrearranged product suggested the participation of an intermediate symmetrical with respect to carbons 1 and 2. They considered the most likely intermediate to be benzyne, which would enter into the mechanism as shown in sequence II.

<sup>1</sup>Manuscript received July 11, 1960.

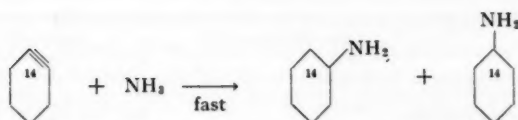
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.

<sup>2</sup>Holder of a National Research Council bursary, 1955-56.

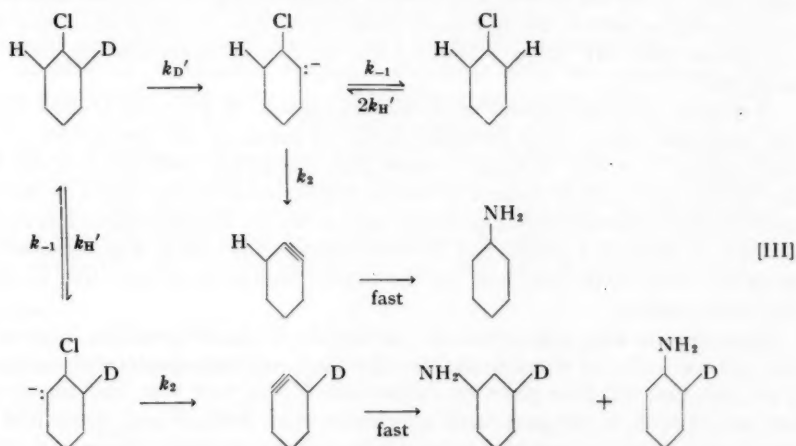




[II]



The existence of a symmetrical intermediate was further indicated when Roberts and co-workers (6) reported in 1956 that chlorobenzene-1-<sup>14</sup>C, bromobenzene-1-<sup>14</sup>C, and iodobenzene-1-<sup>14</sup>C with potassium amide all give aniline-1-<sup>14</sup>C and aniline-2-<sup>14</sup>C in approximately equal quantities. They also studied the reaction of ortho-deuterated fluoro-, chloro-, and bromo-benzene by aminating mixtures of deuterated and undeuterated halobenzenes and comparing the percentage of deuterium before reaction with that after partial reaction. In deuterated bromobenzene the percentage of deuterium increased with the percentage of reaction indicating that the undeuterated material reacts faster, and the isotope effect,  $i = k_{\text{H}}/k_{\text{D}}$ , was found to be about 5.5. Fluorobenzene-2-<sup>2</sup>H was found to exchange deuterium with the solvent very rapidly. Dilute solutions of chlorobenzene-2-<sup>2</sup>H in chlorobenzene showed a small increase in deuterium content after partial reaction while concentrated solutions showed a decrease. This was taken to mean that chlorobenzene-2-<sup>2</sup>H exchanges deuterium with the solvent at a rate comparable with the amination. On the basis of these and other observations the mechanism III was postulated for the amination and exchange of chlorobenzene-2-<sup>2</sup>H.



[III]

Before the appearance of Roberts' second paper the authors had performed some experiments intended to distinguish between mechanisms I and II by finding out whether or not deuterium is lost from the aromatic ring when chlorobenzene-2-<sup>2</sup>H is aminated by sodamide in liquid ammonia. Mechanism I predicts that chlorobenzene-2-<sup>2</sup>H should

give aniline- $^3\text{H}$  with the same total deuterium content, while mechanism II predicts aniline- $^3\text{H}$  with a smaller deuterium content than the starting material. The results of these preliminary experiments are shown in Table I.

TABLE I  
Atom per cent deuterium in the labelled positions of reactants and products

Experiment	Chlorobenzene- $2\text{-}^3\text{H}$		Aniline- $^3\text{H}$		2,4,6-Tribromoaniline†
	Initial*	Final*	Initial*	Final*	
1. Aniline recovered by acid extraction	—	—	$84.7 \pm 2.0^\ddagger$	$81.9 \pm 0.3^\ddagger$	—
2. Aniline recovered by distillation	—	—	$84.7 \pm 2.0^\ddagger$	$83.6 \pm 1.2^\ddagger$	—
3. Chlorobenzene and 1.7 moles sodamide	$64.3 \pm 1.9$	—	—	$35.4 \pm 0.1$	—
4. Chlorobenzene and 1.7 moles sodamide	$64.3 \pm 1.9$	—	—	$30.8 \pm 1.2$	17.3
5. Chlorobenzene and 1.7 moles sodamide	$64.3 \pm 1.9$	—	—	$30.4 \pm 0.1$	16.3
6. Chlorobenzene and 0.5 mole sodamide	$44.1 \pm 1.5$	$44.1 \pm 1.8$	—	—	—

\*Mean of three analyses  $\pm$  maximum deviation.

†One analysis.

‡This material is probably a mixture of 2-, 2,4-, and 2,4,6-deuterated aniline but the analyses are calculated on the assumption that it is aniline- $^3\text{H}$ .

Experiments 1 and 2, Table I, were intended to find out whether or not ring-deuterated aniline exchanges hydrogen isotopes with the reaction mixture or during recovery and purification. In experiment 1 a sample of aniline partially deuterated in the ortho and para positions was treated with sodamide in liquid ammonia and recovered by Bergstrom's method (1) which involves extraction of aniline from the reaction mixture with aqueous hydrochloric acid. It is seen that some deuterium was lost by this procedure. In experiment 2 the use of acid was avoided by extracting the reaction mixture with ether and recovering aniline by fractional distillation. The recovery of aniline was reduced by almost half but Table I shows that the loss of deuterium by this method was negligible.

A mixture of chlorobenzene and chlorobenzene- $2\text{-}^3\text{H}$  was then treated with 1.7 times the equivalent quantity of sodamide in liquid ammonia and the aniline was recovered. Experiments 3, 4, and 5, Table I, show that the aniline produced contained about half the deuterium originally present in the starting material. This aniline was then brominated and the 2,4,6-tribromoaniline produced was analyzed for deuterium. Experiments 4 and 5, Table I, show that almost half the deuterium in the aniline was displaced by bromine so that a little more than half the deuterated aniline must have had its deuterium in the meta position.

These results were taken to favor mechanism II since it predicts a loss of deuterium and the formation of equal quantities of ortho- and meta-deuterated aniline. However, if the reaction did take place by mechanism II, the fact that half the deuterium was lost would lead to the surprising conclusion that protium and deuterium are lost at equal rates. A further test of this point was made by reacting a mixture of chlorobenzene and chlorobenzene- $2\text{-}^3\text{H}$  with half the equivalent quantity of sodamide and recovering the unreacted chlorobenzene. The data from experiment 6, Table I, show that there was no change in the deuterium content of the chlorobenzene, which seemed to confirm that protium and deuterium react at equal rates.

With the appearance of the second paper by Roberts and co-workers (6) it was evident

that our results could be accounted for by mechanism III in a very particular combination of circumstances. As the reaction proceeds, the usual isotope effect tends to increase the deuterium in the unreacted chlorobenzene and the product aniline, but exchange would tend to decrease it, so that a suitable combination of rate of amination, rate of exchange, initial concentration of deuterium, and percentage of reaction could result in a 50% loss of deuterium and no change in the deuterium content of the chlorobenzene. Since Roberts and co-workers did not measure the deuterium in their aniline and we did not measure the deuterium in our unreacted chlorobenzene it was not possible to determine whether or not the combination of factors necessary to fit our data to mechanism III actually existed. Since the fit of Roberts' own data to mechanism III was far from precise, it seemed worth while to repeat and extend our experiments to include in one set of reactions all the measurements necessary for a test of the mechanism.

### EXPERIMENTAL

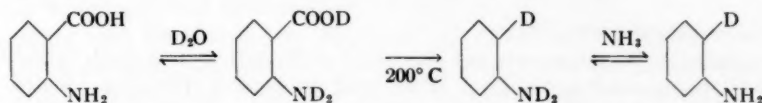
#### *Chlorobenzene-2-<sup>2</sup>H*

Grignard reagent was prepared from 194 g of Eastman Kodak white label *o*-chloriodobenzene (0.814 mole) in a flame-dried flask under an atmosphere of dry nitrogen. Acid titration of the solution indicated 90–97% yields. In the preliminary experiments the Grignard was decomposed by adding 1.63 g of deuterium oxide\* (0.814 mole) very slowly with vigorous stirring. Gilman's color test I (7) was negative at the end of the addition. The solution was then washed with water and dried over anhydrous potassium carbonate. The product was recovered from the ether layer by fractionation through a 10-cm Vigreux column. Yields ranged from 45% to 65%, b.p. 128–132° C at 742 mm,  $n_D^{21.8} = 1.5261$ . Deuterium analyses averaged about 80% chlorobenzene-2-<sup>2</sup>H.

Since Roberts and co-workers reported the preparation of pure chlorobenzene-2-<sup>2</sup>H (without stating the method of analysis) by decomposing *o*-chlorophenylmagnesium iodide with deuterioacetic acid, this method was tried. To the Grignard reagent prepared as described above was added 112.4 g (1.84 mole) of deuterioacetic acid slowly with vigorous stirring. At the end of the addition Gilman's color test I was negative (7). Water was added to dissolve the magnesium salts and the ether layer was separated. The ethereal solution was washed with sodium hydroxide to remove excess acetic acid, dried over anhydrous calcium sulphate, and distilled through an approximately 20-plate column. The yield of chlorobenzene was 49.6 g (53.8%), b.p. 130.0–130.5° C at 745 mm,  $n_D^{25} = 1.5209$ . This material analyzed 81.6% chlorobenzene-2-<sup>2</sup>H. Two samples of deuterioacetic acid were used with identical results; one sample was prepared by hydrolyzing freshly distilled acetic anhydride with deuterium oxide, the other was obtained from Merck and was certified by the supplier to contain more than 98% deuterioacetic acid.

#### *Deuterated Aniline*

The preparation of aniline-2-<sup>2</sup>H was attempted by the decarboxylation of deuterated anthranilic acid as shown in the following sequence of reactions.



Decarboxylation of aromatic acids with calcium deuterioxide at 500° C has been shown

\*Obtained from the Commercial Products Division of Atomic Energy of Canada Ltd., and reported by the supplier to contain 99.83 atom% deuterium.

to give a mixture of isomerically deuterated products (8), but it was thought that the mild conditions possible in the decarboxylation of anthranilic acid might permit success.

Thirty grams of anthranilic acid (0.219 mole) was dissolved in 70 ml of dioxane in a distilling flask and 6.6 g of deuterium oxide (0.330 mole) was added. After the solution had stood for 160 hours at room temperature the solvents were removed under vacuum. A condenser and receiver were attached to the distilling flask and the latter was heated in an oil bath at 200–210° C until no more aniline distilled over. This crude aniline was redistilled to give 16.2 g of product (85% yield), b.p. 179–183° C at 742 mm,  $n_D^{21.3} = 1.5826$ . Deuterium analyses of the aniline obtained from two runs, A and B, gave the atom per cent deuterium in product A =  $21.2 \pm 0.5\%$  and in product B =  $12.0 \pm 0.1\%$ . (These analyses would correspond to an aniline- $^3\text{H}_3$  content of  $49.4 \pm 1.2\%$  in A and  $27.9 \pm 0.2\%$  in B.) In order to remove deuterium from the amino group of the aniline, it was twice dissolved in about 500 ml of liquid ammonia and allowed to stand until the ammonia had evaporated. Distillation gave aniline, b.p. 60–65° C at 2.5 mm,  $n_D^{21.3} = 1.5834$ , in which the intensity of the NH stretching overtone at 1498  $\text{m}\mu$  matched that of ordinary aniline.\* Analysis showed  $12.1 \pm 0.3$  at. % deuterium in A and  $6.66 \pm 0.02$  at. % in B. (This would correspond to an aniline- $2\text{-}^2\text{H}$  content of  $84.7 \pm 2.0\%$  in A and  $46.6 \pm 0.1\%$  in B.)

These results show that the deuterated aniline obtained by decarboxylating partially deuterated anthranilic acid has a little more than half its deuterium in the ring instead of one-third as predicted for a statistical distribution, or less than one-third as would be expected if there were a normal isotope effect in the decarboxylation. This requires that the decarboxylation take place by a mechanism such that either deuterium migrates in preference to protium or deuterium enters more than one position in the ring. The latter possibility seems much the more likely, especially in view of the observation (8) that this actually happens with simple aromatic acids on decarboxylation with  $\text{Ca}(\text{OD})_2$ . In order to find out how general the redistribution of deuterium is, some of the aniline from run B was converted to 2,4,6-tribromoaniline as described below. This tribromoaniline contained no deuterium so the most likely hypothesis is that decarboxylation gives a mixture of aniline- $2\text{-}^2\text{H}$ , aniline- $2,4\text{-}^2\text{H}_2$ , and aniline- $2,4,6\text{-}^2\text{H}_3$ .

#### 2,4,6-Tribromoaniline

To determine the fraction of deuterium in the meta position of the deuterated aniline obtained by decarboxylation or by amination the sample in question was brominated and the 2,4,6-tribromoaniline was analyzed for deuterium. This method has been used previously by Lauer and Errede (9). About 1.0–1.5 g of deuterated aniline was dissolved in 20 ml of water. The solution was cooled in ice and a solution of bromine in ethanol (25% by weight) was added from a burette until the first appearance of a permanent yellow tinge. The precipitate was filtered, washed with water, dissolved in alcohol, and reprecipitated by the addition of water. The material obtained in this way melted sharply at 118° C (uncorr.) and was analyzed for deuterium as described below.

#### Amination of Chlorobenzene- $2\text{-}^2\text{H}$

In the preliminary experiments the procedure of Bergstrom was used. Sodamide was prepared by the method of Vaughan, Vogt, and Nieuwland (10) from 5.2 g of sodium (0.226 g-atom) in about 600 ml of liquid ammonia. When the blue color of the metal solution had turned to the grey of sodamide, 15 g of chlorobenzene- $2\text{-}^2\text{H}$  (0.133 mole)

\*Spectral measurements were made on a Beckman spectrophotometer model DK-1.

was added dropwise over a period of 20 minutes. After another 40 minutes, 11 g of ammonium chloride (0.202 mole) was added and the solvent was allowed to evaporate overnight. Ether was added to the residue and refluxed to drive off residual ammonia. The ether-insoluble salt was dissolved in water and the aniline was extracted from the aqueous layer with ether. The ether solution was dried over anhydrous potassium carbonate, and the aniline was recovered by repeated fractionations through a 10-cm Vigreux column at 60–65° C at 20 mm. Purity of the aniline was checked by comparison of the intensity of the 1498  $m\mu$  peak with that of pure aniline. Yields of pure product averaged about 25% by this method of recovery. Bergstrom's method of acid extraction gave yields of 40% but could not be used because of the danger of exchange between the acid and ring hydrogen. Deuterium analyses on the product were carried out as described below.

In later experiments, where it was desired to isolate unreacted chlorobenzene as well as aniline, Roberts' procedure was used. The chlorobenzene-2- $^2\text{H}$  in 150 ml of liquid ammonia was added to the sodamide solution over a period of 1 minute. Three minutes after the addition was complete the reaction was stopped by the addition of 20 g of ammonium nitrate (0.250 mole) dissolved in 100 ml of liquid ammonia. Anhydrous ether, 150 ml, was added to the reaction mixture and the ammonia was allowed to evaporate overnight. Then 200 ml of water was added and stirred for 10 minutes. The ether layer was separated and washed with water. The aqueous layer and washings were boiled to remove excess ammonia and ether, then analyzed for chloride by the Volhard method. The ethereal solution was dried over anhydrous calcium sulphate, then distilled. Fractionation through a 13-cm Vigreux column gave aniline, b.p. 55–65° C at 4–5 mm,  $n_D^{25} = 1.5836$ , and chlorobenzene, b.p. 130.0–130.5° C at 754 mm,  $n_D^{25} = 1.5207$ . The initial separation of aniline and chlorobenzene was most convenient at reduced pressure but the final purification of chlorobenzene was done at atmospheric pressure in a 20-plate column. Each substance was shown to be free of the other by its infrared spectrum. Each was analyzed for deuterium as described below.

#### *Deuterated Aniline under Amination Conditions*

In order to determine whether or not aniline loses deuterium after it is produced in the reaction or during recovery, the first amination procedure was repeated exactly except that the deuterated aniline obtained from the decarboxylation of anthranilic acid was used instead of chlorobenzene. The results are shown as experiments 1 and 2, Table I.

#### *Deuterium Analyses*

The samples were burned in a standard macrocombustion apparatus using a Vycor tube and a plug of silver wire to trap halogens. The water of combustion was collected in a Dry Ice trap and treated with clean copper wire to remove halogens, or barium carbonate, to remove soluble oxides of nitrogen. It was then purified by the method of Keston, Rittenberg, and Schoenheimer (11) except that calcium oxide and potassium permanganate were used instead of potassium hydroxide and chromium trioxide. The density of the water of combustion was determined by the gradient density tube method described by Anfinson (12). This gives the weight per cent,  $w$ , of deuterium oxide in the water of combustion. From this the atom per cent deuterium in the labelled positions of the molecule was calculated by the equation

$$\text{atom per cent deuterium in } n' \text{ positions} = (n/n') \cdot 900w/(1000-w),$$



where  $n'$  = number of labelled positions in the molecule and  $n$  = total number of hydrogen atoms in the unlabelled molecule.

In the case of chlorobenzene, combustion analyses were supplemented by spectrophotometric analyses using a Perkin-Elmer model 21 spectrophotometer. Measurements were made at  $10.115\ \mu$  with slit width  $160\ \mu$  and at  $10.555\ \mu$  with slit width  $248\ \mu$ . These correspond to spectral slit widths of  $0.020\ \mu$  and  $0.028\ \mu$  respectively. All measurements were made by the base-line technique in  $0.025$ -mm cells. Mixtures of chlorobenzene and the  $81.6\%$  chlorobenzene- $2\text{-}^3\text{H}$  described above gave linear Beer's law plots which were used to analyze the chlorobenzene obtained from the amination reactions. Table II shows the data for standard mixtures and Table III shows those for reaction products.

TABLE II  
Infrared analyses of known mixtures of chlorobenzene and chlorobenzene- $2\text{-}^3\text{H}$

Mole % chlorobenzene- $2\text{-}^3\text{H}$	Wavelength	$I_0^\dagger$	$I^\ddagger$	$\log I_0/I$
$81.6 \pm 1.9^*$	10.115	82.1	45.5	0.256
	10.555	84.2	61.3	0.140
$69.5 \pm 1.6$	10.115	82.5	49.7	0.220
	10.555	84.0	63.7	0.120
$55.3 \pm 1.3$	10.115	82.6	56.0	0.169
	10.555	83.8	68.4	0.0881
$41.8 \pm 1.0$	10.115	82.5	62.0	0.125
	10.555	83.4	72.7	0.0597
$27.8 \pm 0.6$	10.115	82.3	69.0	0.0766
	10.555	83.2	77.0	0.0336
$16.4 \pm 0.4$	10.115	82.7	74.9	0.0430
	10.555	83.5	81.3	0.0116

\*Determined by combustion.

$^\dagger\%$  Transmission at the base line.

$^\ddagger\%$  Transmission at the peak.

TABLE III  
Infrared analyses of chlorobenzene - chlorobenzene- $2\text{-}^3\text{H}$  mixtures obtained from amination reactions

Run	Wavelength	$I_0^*$	$I^\dagger$	$\log I_0/I$	Mole % $o\text{-DC}_6\text{H}_4\text{Cl}^\ddagger$	Average mole % $o\text{-DC}_6\text{H}_4\text{Cl}$
1	10.115	82.4	64.5	0.106	35.8	$35.0 \pm 0.8$
	10.555	83.8	75.0	0.0481	34.3	
2	10.115	83.7	62.0	0.130	42.7	$41.3 \pm 1.4$
	10.555	83.8	72.9	0.0605	40.0	
3	10.115	82.9	67.1	0.0919	28.5	$29.0 \pm 0.5$
	10.555	83.5	76.0	0.0405	29.5	
4	10.115	82.4	70.8	0.0660	23.5	$22.7 \pm 0.9$
	10.555	83.3	78.6	0.0252	21.8	

\*% Transmission at the base line.

$^\dagger\%$  Transmission at the peak.

$^\ddagger$  Calculated from  $\log I_0/I$  and the data of Table II.

## RESULTS AND DISCUSSION

Roberts and co-workers (6) derived a kinetic expression from mechanism III to account for the change in deuterium content of chlorobenzene during amination. It will be necessary to reproduce their derivation in order to extend it to cover the deuterium content of the aniline produced in the reaction.

If  $k_2$  is large compared with  $k_H'$  and  $k_D'$ , as seems likely, the rate of disappearance of deuterated chlorobenzene, D, is given by the expression

$$\frac{-d[D]}{dt} = (k_H' + k_D')[D][NH_2^-] - k_{-1}[\text{anion B}].$$

Application of the steady-state approximation to anion B gives

$$[\text{anion B}] = \frac{k_H'}{k_{-1} + k_2}[D][NH_2^-],$$

which converts the preceding expression to

$$\frac{-d[D]}{dt} = (k_H' + k_D')[D][NH_2^-] - \frac{k_{-1}k_H'}{k_{-1} + k_2}[D][NH_2^-].$$

By a similar process the rate of disappearance of chlorobenzene, H, is found to be

$$\frac{-d[H]}{dt} = 2k_H'[H][NH_2^-] - \frac{k_{-1}}{k_{-1} + k_2}(2k_H'[H][NH_2^-] + k_D'[D][NH_2^-]).$$

Letting the isotope effect,  $k_H'/k_D' = i$ , and the fraction of anion returning to starting material,  $k_{-1}/(k_{-1} + k_2) = F$ , division of one rate expression by the other gives

$$\frac{d[D]}{d[H]} = \frac{[i(1-F)+1][D]}{2i(1-F)[H]-F[D]}.$$

Integration of this expression yields

$$[1] \quad \ln \left[ \frac{[D]_t}{[D]_0} \right] + \frac{1+i-F}{1-i+F} \ln \left[ \frac{(-1+i-F)\frac{[H]_t}{[D]_t} - F}{(-1+i-F)\frac{[H]_0}{[D]_0} - F} \right] = 0.$$

Roberts' equation [1] can be more conveniently applied by setting the fraction of chlorobenzene deuterated at time  $t = d$ , and the fraction of starting material which has reacted at time  $t = P$ . Equation [1] then becomes

$$[2] \quad \log \frac{d}{d_0}(1-P) = \frac{i(1-F)+1}{i(1-F)-1} \log \frac{(1/d)-1-[F/\{i(1-F)-1\}]}{(1/d_0)-1-[F/\{i(1-F)-1\}]}.$$

Equation [1] or [2] concerns only the change in concentration of deuterium in unreacted chlorobenzene. In order to calculate the aniline composition predicted by mechanism III it is necessary to extend the kinetic treatment as follows. Let  $A_D$  and  $A_H$  represent deuterated and undeuterated aniline, respectively,

$$\frac{d[A_D]}{dt} = k_2[B],$$

$$\frac{-d[D]}{dt} = (k_H' + k_D')[D][NH_2^-] - k_{-1}[B].$$

Dividing one rate by the other gives

$$\frac{-d[A_D]}{d[D]} = \frac{k_2[B]}{(k'_H + k'_D)[D][NH_2^-] - k_{-1}[B]}.$$

Substituting the steady-state expression for B and introducing  $i$  and  $F$ , where appropriate, gives

$$\frac{-d[A_D]}{d[D]} = \frac{i(1-F)}{i(1-F)+1}.$$

Integrating with the condition that  $[A_D] = 0$  when  $[D] = [D]_0$  gives

$$[A_D] = \frac{i(1-F)}{i(1-F)+1}([D]_0 - [D]).$$

If it is assumed that  $([A_D] + [A_H])/([D]_0 + [H]_0) = P$  and that  $([D] + [H])/([D]_0 + [H]_0) = 1 - P$  the above expression becomes

$$\frac{[A_D]}{[A_D] + [A_H]} = \frac{1}{P} \frac{i(1-F)}{i(1-F)+1} \frac{[D]_0}{[D]_0 + [H]_0} - (1-P) \frac{[D]}{[D] + [H]}.$$

This expression is simplified by letting the fraction of aniline which is deuterated =  $a$ , and the fraction of chlorobenzene which is deuterated =  $d$ , which gives

$$[3] \quad a = \frac{i(1-F)}{i(1-F)+1} \frac{d_0 - d(1-P)}{P}.$$

Equations [2] and [3] were used to calculate  $a$  and  $d$  according to mechanism III and the results are compared with the experimental results in Table IV. The  $F$  values shown in Table IV were calculated from equation [2] using Roberts' value of  $i = 5.7$ . The constancy of  $F$  through four different runs is strong support for the Roberts' mechanism of concurrent amination and exchange. The average value of  $0.864 \pm 0.020$  is much more precise than the  $0.56 \pm 0.20$  reported by Roberts and co-workers (6). The different magnitudes of  $F$  in the two investigations may be due to some difference in experimental conditions, such as the fact that potassium amide was used in one case and sodamide in the other, or it may be the result of a difference in the method of analyzing chlorobenzene for deuterium. A spectrophotometric method was used in both cases and the standard sample on which all the analyses rest was prepared in the same way in both investigations. In our case the standard sample analyzed 81.6% chlorobenzene-2-<sup>3</sup>H by combustion, while in Roberts' case the standard sample was reported to be 100% chlorobenzene-2-<sup>3</sup>H without mention of the method of analysis. If the two standard samples are assumed to be both about 80% deuterated then the two ranges of  $F$  values overlap, although the precision of the set by Roberts and co-workers is not improved.

The  $a$  values in Table IV were calculated from equation [3] using  $i = 5.7$  and the calculated values of  $F$ . Comparison of the calculated and observed values of  $a$  shows that the former is lower by about 10% in each case. Although the  $a$  values calculated for Roberts' mechanism are low, they parallel the observed values so closely as to leave little room for doubt that the mechanism is essentially correct.

The 10% discrepancy is probably due largely to the method of determining  $P$  by measuring the moles of chloride ion produced. Bergstrom and co-workers (1) showed

TABLE IV  
Amination of mixtures of chlorobenzene and chlorobenzene-2-<sup>3</sup>H

Run	$d_0^{*†}$	$d^{*†}$	$P^{*§}$	$F_{calc}  $	$a_{calc}^{***}$	$a_{obs}^{***}$
1	0.407 ± .003	0.350 ± .008	0.452 ± .006	0.844 ± .011	—	—††
2	0.816 ± .019	0.414 ± .014	0.718 ± .006	0.870 ± .005	0.416 ± .004	0.441 ± .000
3	0.594 ± .014	0.290 ± .005	0.819 ± .012	0.868 ± .001	0.283 ± .004	0.326 ± .005
4	0.396 ± .009	0.227 ± .009	0.783 ± .007	0.874 ± .005	0.185 ± .001	0.204 ± .003

\*Each datum is the mean of three analyses ± the maximum deviation from the mean.

† $d_0$  = mole fraction chlorobenzene-2-<sup>3</sup>H at zero time.

‡ $d$  = mole fraction chlorobenzene-2-<sup>3</sup>H at time  $t$ .

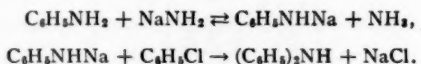
§ $P$  = mole fraction starting material converted to chloride ion at time  $t$ .

|| The maximum value was calculated from equation [2] using the minimum value of  $d$  and the maximum values of  $d_0$  and  $P$ ; the reverse combination gave the minimum value.

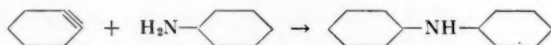
\*\*\* The maximum value was calculated from equation [3] using the minimum value of  $d$  and the maximum values of  $d_0$ ,  $P$ , and  $F$ .

†† Not enough product for analysis.

that the aniline produced by amination of chlorobenzene is always accompanied by by-products, among which they identified diphenylamine, triphenylamine, and *p*-aminobiphenyl. They suggested that these are formed from aniline as illustrated in the following equations:



It is seen that these side reactions produce chloride ion while consuming both chlorobenzene and aniline in a manner not included in the Roberts' mechanism. Since the side reactions should consume ring-deuterated and undeuterated reactants at equal specific rates, they will not alter the mole fraction of deuterated chlorobenzene,  $d$ , or aniline,  $a$ , but they will make the apparent percentage of reaction,  $100P$ , too large. Insertion of the experimental values of  $a$ ,  $d$ ,  $d_0$ , and  $i = 5.7$  into equations [2] and [3] give calculated  $P$  values of 0.646, 0.647, and 0.648 in runs 2, 3, and 4, Table IV, respectively. While the precision of the calculated  $P$  values among runs is probably largely fortuitous, they show that a reasonable amount of side reaction of the type proposed by Bergstrom could account for the low calculated  $a$  values. A more attractive mechanism for the formation of by-products within the Roberts' mechanism would be the following:



but the effect on  $a$  would be the same as that suggested for the Bergstrom mechanism.

In summary, our data and the predictions of Roberts' mechanism of concurrent amination and exchange are in excellent agreement on the deuterium content of partially reacted chlorobenzene, on the ortho-to-meta ratio of the deuterated aniline produced, and in reasonable agreement on the total deuterium content of the aniline. There can be little doubt that the mechanism is essentially correct.

A referee has pointed out that the excess of aniline-3- $^2\text{H}$  over aniline-2- $^2\text{H}$  (56% and 54% of the former in experiments 4 and 5, Table I) suggests a secondary isotope effect on the rates of addition of ammonia to benzyne-2- $^2\text{H}$ . Roberts and co-workers (13) have observed that inductive electron withdrawal by the substituent in a 2-substituted benzyne favors the formation of 3-substituted addition products. This would indicate that deuterium has a  $-I$  effect, as has been suggested by Shiner on other grounds (14). The agreement of our data with Shiner's prediction is interesting, but we doubt whether the accuracy of the analysis warrants a definite conclusion.

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# THE STRUCTURE OF THE "GUM ASAFOETIDA" POLYSACCHARIDE<sup>1</sup>

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## ABSTRACT

The polysaccharide from gum asafoetida contains D-galactose, L-arabinose, L-rhamnose, 4-O-methyl-D-glucuronic acid, and D-glucuronic acid. It is a highly branched polymer which contains a backbone of D-galactopyranose residues which are very probably mainly 1,3- $\beta$ -linked.

The side chains consist of residues of L-arabinofuranose, D-galactopyranose, D-glucuronic acid, and its 4-O-methyl ether.

## INTRODUCTION

Oleogum resins such as asafoetida (1), frankincense (2), and myrrh (3) consist in the main of a mixture of polysaccharide and aromatic substances. The impure carbohydrate portion remains when the crude gum is extracted with a solvent such as methanol. It may be purified by pouring its clarified aqueous solution into alcohol. Application of the above procedure to gum asafoetida gave the neutral salt (equiv. wt. 1500) of the polysaccharide as a white powder, readily soluble in cold water to form a conducting solution, which possessed a negative optical rotation ( $-48^\circ$ ). All attempts to fractionate it were unsuccessful and it was concluded that the polysaccharide was homogeneous. Acidic hydrolysis yielded a mixture of sugars which were characterized as D-galactose, L-arabinose, L-rhamnose, and D-glucuronic acid together with its 4-O-methyl derivative and were present in the approximate proportions 5:3:trace:1. Somewhat different figures (14.2%, 26.5%, 1.7%, 17.1% respectively) were obtained by Bézanger-Beauquesne and Chosson (4).

When the polysaccharide was partially broken down by acid, small amounts of two neutral disaccharides and larger amounts of two aldobiouronic acids were isolated. The neutral oligosaccharides were not obtained crystalline; they yielded D-galactose only on hydrolysis and were tentatively characterized by their rates of movement on chromatograms and by the infrared absorption spectra of their acetates (5) as 6-O- $\beta$ -D-galactopyranosyl-D-galactose (6) and the 3-O- $\beta$ -D-galactopyranosyl-D-galactose. Both the acidic disaccharides give D-galactose on hydrolysis, that which moved faster on the chromatogram also yielded 4-O-methyl-D-glucuronic acid, which was characterized as the amide of 4-O-methyl methyl- $\alpha$ -D-glucuronoside (7). The slower-moving aldobiouronic acid yielded D-glucuronic acid on hydrolysis. Both, after methylation, reduction with lithium aluminum hydride, and further methylation, followed by hydrolysis, gave 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4-tri-O-methyl-D-galactose and were therefore identified because of their low positive rotations as 6-O-( $\beta$ -D-glucopyranosyluronic acid)-D-galactose (8) and as 6-O-(4-O-methyl- $\beta$ -D-glucopyranosyluronic acid)-D-galactose (9). When the acidic, ash-free, polysaccharide was dissolved in water and the solution heated autohydrolysis occurred with the liberation of L-arabinose and L-rhamnose together with traces of D-galactose and oligosaccharides, leaving a degraded gum which contained D-galactose, D-glucuronic acid, and its 4-O-methyl derivatives, and traces (ca. 5%) of L-arabinose. Hydrolysis of the gum with 0.1 *N* hydrochloric acid at 100° for 17 hours

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failed to remove all the L-arabinose residues. The degraded gum at this stage contained a galactose-to-arabinose ratio of approximately 15 to 1. It is possible therefore that some of the pentose residues were in the pyranose form.

Methylation experiments showed that both the original polysaccharide and the degraded polysaccharide were of the branched chain type. The methylated sugars isolated were identified as 2,3,5-tri-*O*-methyl-L-arabinose, 2,3,4,6-tetra-, 2,4,6-tri-, 2,4-di-, and 2-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-D-glucuronic acid. The 2-*O*-methyl-D-galactose derivative was not encountered in the products of hydrolysis of the degraded gum. An L-rhamnose derivative and an L-arabinose (?) derivative remain to be identified in the products of hydrolysis of the undegraded gum. The amounts of sugars were determined by the hypiodite method of Hirst, Hough, and Jones (10) and were found to be present in the following approximate molecular proportions in the methylated original polysaccharide: 2,3,5-tri-*O*-methyl-L-arabinose plus 2,3,4,6-tetra-*O*-methyl-D-galactose (end groups), (3 + tr. parts); dimethyl-L-arabinose (?) (small); 2,4,6-tri- (2 parts), 2,4-di- (2 parts), and 2-mono-*O*-methyl-D-galactose (1 part); and 2,3,4-tri-*O*-methyl-D-glucuronic acid (1 part). The methylated degraded gum gave the neutral sugars 2,3,5-tri-*O*-methyl-L-arabinose; 2,3,4,6-tetra-*O*-methyl-, 2,4,6-tri-*O*-methyl-, 2,4-di-*O*-methyl-D-galactose; and 2,3,4-tri-*O*-methyl-D-glucuronic acid in the approximate proportion of 1:2:9:6:5. An aqueous solution of the gum was oxidized with sodium metaperiodate solution (cf. 10a) and yielded 0.11 mole of formic acid with the consumption of 0.65 mole of metaperiodate per sugar residue (calc. as  $C_6H_{10}O_5$ ) in 30 hours. These figures show that for every sugar oxidized with the formation of formic acid, four other sugars were oxidized and that, in all, approximately half the sugar residues in the polysaccharide were destroyed by the reagent. This supposition is in fair agreement with the methylation results.

Some overoxidation of the polysaccharide would occur because of the presence of end groups of D-glucuronic acid but it is believed that this would not be great because (ca. 75% of) the D-glucuronic acid residues were substituted at  $C_4$  by methoxyl groups which would prevent the formation of an easily overoxidized intermediate. It is assumed that formyl ester production was small.

The degraded gum consumed 0.83 mole of periodate with the production of 0.26 mole of formic acid (per  $C_6H_{10}O_5$ ). Therefore, apparently approximately 75% of the polysaccharide was oxidized and a little over a quarter of the sugar residues were present as end groups which would yield formic acid. These results are not in good agreement with those obtained by the methylation procedure, which indicates that 33% of the polysaccharide should be oxidized and that approximately 20% of the sugars contain hydroxyl groups on each of three contiguous carbon atoms. The reason for the discrepancy is not clear but it may be due to an excess of consumption of metaperiodate at the reducing end of the polysaccharide or to "overoxidation".

The gum was degraded by first oxidizing it with sodium metaperiodate to a polyaldehyde as described above which was reduced with sodium borohydride to the polyalcohol. The product was then degraded by the action of cold dilute acid (Smith *et al.* (11), cf. 11a, 11b). The degraded polysaccharide was isolated when its solution was poured into ethanol. This material gave galactose and arabinose (ca. 5:1) only on complete hydrolysis. It had a slightly branched structure since on further periodate oxidation it yielded a small amount of formic (0.18 mole per  $C_6H_{10}O_5$ ) and consumed some metaperiodate (0.34 mole per  $C_6H_{10}O_5$ ). The alcohol-soluble fraction contained glycerol, ethylene glycol, and glycosides of arabinose and galactose which yielded these sugars on

acidic hydrolysis. The degraded gum when subjected to further degradation in similar fashion gave a galactan ( $[\alpha]_D +31^\circ$ ) which was oxidized to a small extent by periodate (0.21 mole consumed per  $C_6H_{10}O_6$ ) and produced traces (0.08 mole per  $C_6H_{10}O_6$ ) of formic acid only on oxidation with metaperiodate.

These results indicate that the polysaccharide consisted of a main chain of mainly 1,3-linked- $\beta$ -D-galactopyranose residues to which are attached D-galactopyranose, L-arabinofuranose, and L-arabinopyranose (?) residues. The mode of linkage of the last sugar was not identified. To the side chains are attached residues of D-glucuronic acid, its 4-O-methyl ether, L-rhamnose, and D-galactose (all in the pyranose form). It is not possible to give an unambiguous structure for gum asafoetida at this stage. The polysaccharide has a much smaller percentage of uronic acid residues than has that from frankincense (2) or that from myrrh (3).

#### EXPERIMENTAL

Paper chromatography was performed by the descending method on Whatman No. 1 paper. Small-scale qualitative separations were carried out by the method of Hirst, Hough, and Jones (12) on Whatman No. 3MM paper. Larger-scale separations were carried out by partition chromatography on cellulose columns using the method of Hough, Jones, and Wadman (13). Chromatographic separations were also conducted on charcoal columns (14) which consisted of a mixture (1:1 w/w) of activated charcoal (Darco C-60) and "Celite". Charcoal columns were eluted with water and/or ethanol.

The following solvent systems were used to separate the neutral sugars by paper chromatography (all v/v):

- (A) butan-1-ol, ethanol, water (3:1:1);
- (B) butan-1-ol, pyridine, water (10:3:3);
- (C) benzene, ethanol, water (169:15:47).

Acidic solvents were used to separate uronic acids and their derivatives.

- (D) ethyl acetate, acetic acid, water (9:2:2);
- (E) ethyl acetate, acetic acid, formic acid, water (18:3:1:4).

The sugars were detected on paper chromatograms either by spraying them with a 1% solution of *p*-anisidine hydrochloride (15) in butan-1-ol followed by heating the chromatogram, or the chromatogram was sprayed with a 1% solution of silver nitrate in acetone followed by 2% ethanolic sodium hydroxide. The rates of movement of sugars are quoted relative to a standard sugar, e.g.  $R_{Rb}$  and  $R_G$  (relative to rhamnose, and 2,3,4,6-tetra-O-methyl-D-glucose). Paper electrophoresis was carried out in a borate buffer at pH 10 (16). Solutions were concentrated under reduced pressure at ca. 40° C or lower. Optical rotations were measured in water and at  $26^\circ \pm 2^\circ$  (unless otherwise stated).

#### Extraction of the Gum

The crude material consisted of the oleogum resin admixed with sand, bark, and organic debris. This material (707 g) was exhaustively extracted with hot methanol until a sample of the methanol extract gave no turbidity when poured into water. The residue was collected by centrifugation and extracted with water. The brownish-green extracts were concentrated to a volume of 150 ml and poured into ethanol (2 l.) to which hydrochloric acid (5 ml:10 N) had been added. The precipitate was collected (centrifuge), redissolved in ice-cold water (150 ml), and the precipitation procedure repeated twice more. The solid resulting was well washed with ethanol to remove hydrochloric acid, then with ether and was dried under reduced pressure. Yield, 120 g (17%).

#### *Attempted Fractionation of the Polysaccharide*

The polysaccharide (20 g) was dissolved in water (1 liter) and ethanol (500-ml portions) was added with vigorous stirring. The polysaccharide was collected by centrifugation after each addition of ethanol. Four main fractions were obtained. Each fraction had  $[\alpha]_D -48^\circ \pm 2^\circ$ ; equiv. wt.,  $1490 \pm 10$ ; and OMe, 1.6%. Each fraction gave on hydrolysis sugars which moved on paper chromatograms, at the rate of L-arabinose, D-galactose, and L-rhamnose plus 4-O-methyl-D-glucuronic acid.

#### *Use of "Cetavlon" (17)*

The polysaccharide (1 g) was dissolved in water (10 ml) and aqueous "Cetavlon" (20% w/v) was added until precipitation was complete. The precipitate was collected, dissolved in a minimum volume of aqueous sodium chloride (10% w/v), and the solution was poured into ethanol. The precipitate was dissolved in water and dialyzed against tap water until the solution was free from chloride (2 days). The dialyzate was concentrated and poured into two volumes of ethanol. The precipitate was collected, washed with ethanol and ether, and dried. Yield, 0.87 g.

The fraction which was not precipitated by "Cetavlon" was recovered when the solution was concentrated and poured into ethanol. The solid was dissolved in water, the solution dialyzed and recovered as described above. The product weighed 0.04 g. Both fractions had  $[\alpha]_D -48^\circ \pm 2^\circ$  ( $c$ , 1.0) and equiv. wt.  $1500 \pm 10$ .

#### *Preparation of Gum Acetate*

The polysaccharide (5 g) was added, in small portions, to *N,N*-dimethylformamide (100 ml) at  $30^\circ\text{C}$ . After stirring for 1 hour the suspension had dissolved. Pyridine (90 ml) was then added portionwise during 30 minutes followed by acetic anhydride (32 ml) which was added in four equal portions during 4 hours. The solution was stirred for a further 5 hours at  $32^\circ\text{C}$  and then left at  $20^\circ\text{C}$  overnight. The solution was then poured with vigorous stirring into cold hydrochloric acid (1 liter; 2%) plus chopped ice (50 g). The precipitated cream-colored product was collected by filtration, washed well with hydrochloric acid (0.5%), and then with water (250 ml,  $\times 5$ ). The product (8 g) had  $[\alpha]_D -52^\circ$  ( $c$ , 2.0 in  $\text{CHCl}_3$ ). Found:  $-\text{COCH}_3$ , 42%.

The fractionation of this product by the method of Goodban and Owens (18) was attempted and yielded fractions with  $[\alpha]_D -46^\circ \pm 2^\circ$  ( $c$ , 2.0 in  $\text{CHCl}_3$ ) and  $-\text{COCH}_3$ ,  $41 \pm 1\%$ . No fractionation had been achieved.

#### *Autohydrolysis of the Gum Polysaccharide*

The gum (15 g) was obtained in an ash-free form by passing its aqueous solution through columns of ion-exchange material (Amberlite IR-120 and IR-4B). The acidic eluate was concentrated to a small volume and was precipitated by adding its solution to three volumes of ethanol. The precipitate was dissolved in water (750 ml) and the resulting viscous brown solution was heated under reflux on a steam bath.

At intervals samples were withdrawn and were analyzed chromatographically. The darkness of the solution prevented polarimetric observation being taken. L-Arabinose was the first reducing sugar to appear in the autohydrolyzate and no other sugar was detected until after 26 hours, when traces of D-galactose and L-rhamnose were liberated. The solution was then concentrated to a small volume (30 ml) and poured into ethanol with vigorous stirring. The precipitated degraded product was collected, washed with ethanol and acetone, and dried (yield 11 g, 73%). The supernatant solution from the precipitation was concentrated to a syrup which was dissolved in hot methanol and the



solution was filtered first through charcoal and then through celite. Concentration of this filtrate gave crystalline L-arabinose of melting point  $160^{\circ}\text{C}$  and  $[\alpha]_{\text{D}} +105^{\circ}$ .

#### *Further Hydrolyses of the Degraded Polysaccharide*

The degraded polysaccharide (5 g) was dissolved in formic acid solution (1%; 500 ml) and the solution was boiled under reflux for 10 hours. The solution was then evaporated to a syrup which was boiled with water and the solution was again evaporated to hydrolyze formyl esters. This process was repeated several times. Finally the residue was dissolved in water (50 ml) and the solution was poured into ethanol (2 l.) and the precipitate was collected. This product was washed well with ethanol and dried. It had  $[\alpha]_{\text{D}} +2^{\circ}$  (*c*, 1.0). The supernatant was concentrated to a syrup and examined chromatographically. It contained sugars which moved at the rate of galactose, arabinose, and rhamnose (solvent A and B) plus two neutral oligosaccharides and an aldobiouronic acid (solvent E).

The syrup was fractionated on a cellulose column ( $4 \times 30$  cm) using solvent D as the mobile phase and yielded fraction I: L-rhamnose,  $[\alpha]_{\text{D}} +9^{\circ}$  (*c*, 1.0), m.p.  $91^{\circ}\text{C}$ , identical with an authentic sample; fraction II: L-arabinose,  $[\alpha]_{\text{D}} +100^{\circ}$  (*c*, 1.0), m.p.  $160^{\circ}\text{C}$ , not depressed on admixture with an authentic sample; fraction III: D-galactose,  $[\alpha]_{\text{D}} +81^{\circ}$  (*c*, 1.0), m.p.  $119^{\circ}\text{C}$ , indistinguishable from an authentic specimen; fraction IV: had  $R_{\text{galactose}}$  0.61 and behaved like an aldobiouronic acid. It had  $[\alpha]_{\text{D}} +1^{\circ}$  (*c*, 1.0) and equiv. wt. 364 and after hydrolysis with 2 *N* sulphuric acid, yielded sugars which moved at the rates of 4-*O*-methyl-D-glucuronic acid and D-galactose. Fraction V was a neutral oligosaccharide which on hydrolysis with 2 *N* sulphuric acid yielded D-galactose only. Fraction VI was also a neutral oligosaccharide which on hydrolysis with 2 *N* sulphuric acid gave D-galactose only.

#### *Characterization of Fractions V and VI*

Their rates of movement on chromatograms indicated that both these substances were D-galactose-containing disaccharides. Their rates of movement on paper chromatograms in solvents A, B, D, and E and a comparison of their infrared spectra indicated that they were 3- and 6-*O*-β-D-galactopyranosyl-D-galactose. The corresponding acetates (amorphous) were prepared on the microscale by the method of White *et al.* (5) and their infrared absorption spectra were compared with authentic specimens and found to be identical. Neither disaccharide was obtained crystalline.

#### *Large-scale Preparation of Aldobiouronic Acids*

Insufficient quantity of fraction IV was available for characterization and a further quantity was prepared. The original polysaccharide (15 g) was dissolved in water (200 ml) and deionized by passing its solution down columns of ion-exchange resin (Amberlite IR-120).

The eluate was concentrated to a small volume (25 ml) and poured into ethanol (2 liters). The precipitate was collected (centrifuge), and washed with ethanol and acetone, and dried. The dried acidic polymer (8 g) was dissolved in sulphuric acid (800 ml, 2 *N*) and the solution was heated under reflux for 8 hours. Test experiments on small quantities of material had indicated that these conditions gave maximum yields of aldobiouronic acids. The solution was cooled, neutralized ( $\text{BaCO}_3$ ), filtered and the filtrate was concentrated to a small volume and poured into ethanol (five volumes). The barium salts were collected, washed with alcohol, and dried. The ethanol solution on concentration gave a syrup which contained D-galactose, L-arabinose, and L-rhamnose.

The barium salts were dissolved in water, deionized (Amberlite IR-120 resin) and the solution was concentrated. The mixture of monosaccharides and oligosaccharides was separated on a squat charcoal - celite column by the method of Hough *et al.* (19). Elution with water removed the monosaccharides and elution with up to 30% aqueous ethanol displaced two aldobiouronic acids which were not separated from one another. Separation of these was achieved on sheets of Whatman 3MM paper using solvent E for development. The faster-moving component was identical with fraction IV (above) and was identified as 6-*O*-(4-*O*-methyl-D-glucopyranosyl uronic acid)-D-galactose. The slower-moving component was the corresponding unmethylated aldobiouronic acid.

#### *Proof of Structure of the Aldobiouronic Acids*

The acid (fraction IV, 200 mg) was dissolved in water (3 ml) and methylated with dimethyl sulphate (1.5 ml) and sodium hydroxide (30%; 3 ml) in the usual way. The partially methylated acid was isolated and methylated with Purdie's reagent (20). The resultant methylated ester glycoside (180 g) was dissolved in tetrahydrofuran (50 ml) and reduced by the dropwise addition with stirring of a solution of lithium aluminum hydride (600 ml) in tetrahydrofuran (25 ml).

After 24 hours, excess of lithium aluminum hydride was destroyed by the cautious addition first of ethyl acetate and then of water. The slurry was filtered and the filtrate was evaporated to a small volume which was continuously extracted with chloroform. Complete methylation of the disaccharide was achieved, by the gradual addition during 3 hours of dimethyl sulphate (3 ml) to a stirred solution of the syrup in tetrahydrofuran (15 ml) containing pulverized sodium hydroxide (26 g).

After 16 hours water was added to dissolve the solids and the mixture was heated to 80° to decompose dimethyl sulphate. The solution was neutralized, concentrated, and the residual solution exhaustively extracted with chloroform. Concentration of the extracts yielded the methylated neutral disaccharide (138 mg). Found: OMe, 54.2%. Calc. for  $C_{20}H_{38}O_{11}$ : OMe, 54.8%.

The methylated disaccharide (135 gm) was hydrolyzed by boiling its solution in formic acid (50%, 25 ml) for 6 hours, and after evaporation of the formic acid, with boiling hydrochloric acid (*N*; 25 ml), for 4 hours.

The hydrolyzate was neutralized ( $Ag_2CO_3$ ), filtered, and the filtrate was evaporated to a syrup. Paper chromatography of the syrup indicated the presence of three sugars, the two major components were tentatively identified as 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-galactose. A third trace component of  $R_G$  0.84 (solvent A) was not identified. The sugars were separated on 3MM paper and the two major fractions were identified in the usual way. The fast-moving component had  $[\alpha]_D +80^\circ$  (*c*, 1.0) and gave a crystalline *N*-phenylglycosylamine derivative on boiling its solution in ethanol with aniline. The product had a melting point of 116-117° C and  $[\alpha]_D +205^\circ$  (*c*, 1.0 in acetone). Its melting point was not depressed on admixture with authentic 2,3,4,6-tetra-*O*-methyl *N*-phenyl-D-glucosylamine.

The slow-moving syrup ( $R_G$ , 0.69 in solvent A) had  $[\alpha]_D +96^\circ$  (*c*, 1.0). On heating it in ethanol solution with aniline characteristic rhombic crystals of 2,3,4-tri-*O*-methyl-*N*-phenyl-D-galactosylamine were produced,  $[\alpha]_D -50^\circ \rightarrow +46^\circ$  (*c*, 1.0 in methanol), m.p. 169° C not depressed on admixture with an authentic specimen.

The second aldobiouronic acid contained no methoxyl residue and on hydrolysis with sulphuric acid (2 *N*) it yielded D-galactose, D-glucuronic acid, and D-glucurone (chromatographic evidence). It was methylated and then reduced with lithium aluminum

hydride as described above. The product was remethylated then hydrolyzed and yielded 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-galactose characterized as described above.

*Quantitative Determination of Component Sugars Present in the Polysaccharide*

The ash-free gum (40 g) was dissolved in *N* sulphuric acid (10 ml) and the solution was boiled under reflux for 10 hours. The solution was cooled, ribose (10 mg) was added, and the solution was then neutralized ( $\text{BaCO}_3$ ) and filtered. The filtrate was concentrated to a syrup and the sugars were separated on Whatman 3MM paper. The position and quantity of sugars were determined by the method of Hirst, Hough, and Jones (10). Found: arabinose, 33%; rhamnose, 2%. Galactose was not determined.

*Periodate Oxidation of the Undegraded Polysaccharide*

The polysaccharide (100 mg) was dissolved in water (20 ml) and titrated to neutrality with sodium hydroxide (0.01 *N*) using screened methyl red as indicator. Sodium metaperiodate solution (5 ml; 0.3 *M*) was added and the solution was made up to 100 ml. A blank solution was prepared similarly. Oxidation was allowed to proceed in the dark at 20°. The periodate uptake was determined by the method of Willard and Greathouse (20) but using phosphate in place of borate and the formic acid production by the method of Halsall, Hirst, and Jones (21). Found: moles of metaperiodate consumed and moles of formic acid produced per  $\text{C}_6\text{H}_{10}\text{O}_5$ : 0.22, 0.08 (1 hour); 0.32, 0.08 (3 hours); 0.36, 0.10 (6 hours); 0.48, 0.11 (11 hours); 0.57, 0.11 (23 hours); 0.65, 0.11 (36 hours). Acidic hydrolysis of the periodate-oxidized polysaccharide yielded galactose only.

*Periodate Oxidation of the Degraded Polysaccharide*

The degraded polysaccharide (100 mg) was oxidized with sodium metaperiodate solution as described above. Found: (moles of metaperiodate consumed and moles of formic acid produced for  $\text{C}_6\text{H}_{10}\text{O}_5$ ): 0.37, 0.15 (1 hour); 0.45, 0.15 (3 hours); 0.57, 0.15 (6 hours); 0.63, 0.16 (11 hours); 0.73, 0.19 (23 hours); 0.83, 0.26 (30 hours).

When the periodate-oxidized polysaccharide was recovered and hydrolyzed with dilute sulphuric acid galactose was the only sugar which could be detected chromatographically.

*Periodate Oxidation and Degradation of the Gum. Stage I*

The gum (16.2 g) was dissolved in water (100 ml) and oxidized with sodium metaperiodate (25 g) in water (150 ml) during 72 hours at 20° C with stirring. The solution was diluted with methanol (500 ml) and the precipitated salts were removed by filtration. The filtrate was evaporated to a small volume and sodium borohydride (6 g) in water (100 ml) was added to the solution. Sulphuric acid (2 *N*; 100 ml) was added and the mixture was left at 20° C for 18 hours. The solution was neutralized ( $\text{BaCO}_3$ ), filtered, and the filtrate deionized with Amberlite resin 1R-120 (H). The filtrate was concentrated to 25 ml under reduced pressure and poured into ethanol. The precipitate was collected, dried, and weighed; yield, 4.5 g. This product (equiv. wt., 4300) was insoluble in water after it was dried. It contained galactose and arabinose in the approximate ratio of 5 to 1 (chromatographic evidence) and traces of acid. The alcoholic filtrate on concentration yielded a syrup (8 g) which contained glycerol, glycol, and glycosides, which on hydrolysis yielded galactose and arabinose in the approximate ratio of 1 to 1 (chromatographic evidence).

*Periodate Oxidation of the Periodate-degraded Polysaccharide*

The sample (20 mg) was oxidized in a volume of 100 ml by the addition of sodium

metaperiodate solution (0.1 *M*, 5 ml) and water at 4° C in the dark. At intervals samples were withdrawn and the metaperiodate uptake and formic acid production were measured. Found: moles of metaperiodate consumed and moles of formic acid produced per 162 g polysaccharide: 0.27, 0.10 (4 hours); 0.3, 0.14 (6 hours); 0.36, 0.18 (24 hours); 0.40, 0.15 (48 hours); 0.42, 0.15 (72 hours); 0.44, 0.18 (96 hours).

#### *Periodate Oxidation of the Gum. Stage II*

The periodate-oxidized and periodate-degraded gum (3.5 g) was shaken with a solution of sodium metaperiodate (3 g) in water (50 ml) for 6 days at 20° C. The oxidized product was isolated from the clear solution as described above; the substance was reduced with a solution of sodium borohydride (3 g) in water (100 ml). After 24 hours, the solution was acidified with sulphuric acid (2 *N*, 100 ml) and kept at 20° C for a further 24 hours. The solution was then neutralized ( $\text{BaCO}_3$ ), filtered, and the filtrate was deionized (Amberlite ion exchange resin, IR 120-H). The twice-degraded neutral polysaccharide (2 g) was isolated as described above. This material on hydrolysis yielded galactose only (chromatographic evidence) and had  $[\alpha]_D +31^\circ \pm 5^\circ$  (*c*, 1.0). The alcohol-soluble material contained glycerol, glycol, and small quantities of galactose-containing glycosides.

#### *Periodate Oxidation of the Gum. Stage III*

The degraded gum (20 mg) was oxidized at a concentration of 20% with aqueous sodium metaperiodate (0.1 *M*, 5 ml) at 4° C in the dark. Found: moles of periodate consumed and moles of formic acid produced per  $\text{C}_6\text{H}_{10}\text{O}_5$ : 0.17, 0.08 (4 hours); 0.17, 0.08 (14 hours); 0.21, 0.08 (24 hours); 0.23, 0.10 (48 hours); 0.27, 0.12 (72 hours); 0.32, 0.11 (96 hours). Extrapolation to zero time gave an uptake of 0.21 mole of metaperiodate and a formation of 0.08 of formic acid per  $\text{C}_6\text{H}_{10}\text{O}_5$ .

#### *Methylation of the Undegraded Polysaccharide*

The acetylated polysaccharide (11 g) was dissolved in acetone (200 ml) and methylated with dimethyl sulphate and sodium hydroxide in the usual way. The product was dissolved in a mixture of methanol and methyl iodide and the solution was boiled under reflux; silver oxide was added portionwise to the solution. At the completion of the experiment (24 hours) the product was isolated in the usual way. Methylation was completed when the product was dissolved in dry tetrahydrofuran (200 ml), admixed with powdered sodium hydroxide (40 g), and dimethyl sulphate (13.5 ml) added with stirring at 20° C during 24 hours. The product (6 g) was isolated from the aqueous solution by extraction with chloroform, after the solution had been diluted with water, neutralized with dilute sulphuric acid, and dialyzed against tap water to remove salts, and concentrated. The methylated product had  $[\alpha]_D -76^\circ$  (*c*, 1.0 in  $\text{CHCl}_3$ ). Found: OMe, 40.5%. The product was fractionated by extracting it with mixtures of chloroform - light petroleum (b.p. 60-80° C). Two major products were isolated: (1)  $[\alpha]_D -75^\circ$ ; OMe, 42%; and (2)  $[\alpha]_D -76^\circ$  (*c*, 1.0 in  $\text{CHCl}_3$ ); OMe, 42%. The fractions (1 g and 5 g, respectively) were combined and hydrolyzed as described below.

#### *Hydrolysis of Methylated Gum*

The methylated polysaccharide (5 g) was dissolved in formic acid (50%, 400 ml) and the solution was heated under reflux until the optical rotation reached a constant value (+35°). The solvent was removed and the syrupy residue was boiled with water and the solution concentrated. This process was repeated once more. The residue was dissolved in dilute sulphuric acid (2 *N*, 100 ml) and the solution was heated at 100° for 4 hours.



The cooled solution was then neutralized ( $\text{BaCO}_3$ ), filtered, and the filtrate was concentrated to a syrup. The product was dissolved in water and the solution passed down columns of Amberlite ion exchange resins, IR-120 and IR-4B, and the effluent was concentrated to a syrup (4.28 g) which contained neutral sugars only. The acidic sugars (0.64 g) were recovered when the basic resin (IR-4B) was washed with 30% formic acid and the effluent was concentrated.

A quantitative determination of the sugars present in this mixture was made by the method of Hirst, Hough, Jones (10). Found: end group (3 parts); tri-*O*-methyl hexose (2 parts); di-*O*-methyl hexose (2 parts); mono-*O*-methyl hexose (1 part); and methylated uronic acid (end group) (1 part).

#### *Characterization of the Methylated Neutral Sugars*

The syrup (4.28 g) was separated on a cellulose column (50×4 cm) using light petroleum (b.p. 100–120° C):butan-1-ol (7:3) as the mobile phase. Six fractions were obtained: Fraction I had  $[\alpha]_D -30^\circ$  and OMe 47.2% and consisted chromatographically of one component only. A portion (100 mg) of the syrup was oxidized with bromine water in the usual way and the resulting lactone was dissolved in methanolic ammonia to yield crystalline 2,3,5-tri-*O*-methyl-L-arabonamide, m.p. and mixed m.p. 134° C,  $[\alpha]_D -15^\circ$  (c, 1.0). Fraction II was chromatographically pure and had  $[\alpha]_D +108^\circ$  and moved at the same rate as 2,3,4,6-tetra-*O*-methyl-D-galactose in solvent A, B, and C. Found: OMe, 51.9. Calc. for  $\text{C}_{10}\text{H}_{20}\text{O}_6$ : OMe, 52.5%. A portion of the syrup was boiled with ethanolic aniline and yielded 2,3,4,6-tetra-*O*-methyl-N-phenyl-D-galactosylamine, m.p. 192° C, not depressed on admixture with an authentic specimen,  $[\alpha]_D 40^\circ$  (in acetone, equilibrium value). Fraction III was a mixture and was not characterized. Fraction IV moved chromatographically at the same rate as 2,4,6-tri-*O*-methyl-D-galactose and had OMe, 41.6% (calc. for  $\text{C}_9\text{H}_{18}\text{O}_6$ : OMe, 41.9%) and  $[\alpha]_D 87^\circ$ . The derived crystalline N-phenylglycosylamine derivative was identified as 2,4,6-tri-*O*-methyl-N-phenyl-D-galactosylamine, of m.p. 176°, not depressed by an authentic specimen. The infrared spectra of the derivative and of an authentic specimen were identical. Fraction V crystallized. It behaved chromatographically like 2,4-di-*O*-methyl-D-galactose in solvents A, B, and C. It had m.p. 102° C, not depressed on admixture with an authentic specimen and  $[\alpha]_D +130^\circ \rightarrow 86^\circ$  (constant 2 hours) (c, 1.0). The derived N-phenyl-D-galactosylamine had m.p. 215° C and was indistinguishable from an authentic specimen. Fraction VI was a syrup and had the properties of a mono-*O*-methyl hexose. (Found: OMe, 15.8%. Calc. for  $\text{C}_7\text{H}_{14}\text{O}_6$ : OMe, 16%). When nucleated with 2-*O*-methyl-D-galactose the syrup crystallized. The product had m.p. 148° C, not depressed on admixture with an authentic specimen and  $[\alpha]_D +60^\circ \rightarrow 89^\circ$  (2 hours constant) (c, 1.0). The derived N-phenyl-D-galactosylamine had m.p. 163° C and this product was indistinguishable from an authentic specimen.

#### *Characterization of the Acidic Fraction*

This syrupy material moved as one component ( $R_G$  0.84) on a chromatogram (solvent E) and had  $[\alpha]_D +40^\circ$  (c, 1.0). Further hydrolysis with hot dilute acid did not liberate any neutral sugars. The syrup (250 mg) was dissolved in methanolic hydrogen chloride (2%; 20 ml) and boiled under reflux for 8 hours. The solution was then non-reducing to Fehling's solution. The solution was neutralized ( $\text{Ag}_2\text{CO}_3$ ), filtered, and the filtrate was concentrated to a syrup. This was dissolved in dry tetrahydrofuran and the solution was added dropwise to a solution of lithium aluminum hydride (0.1 g) in tetrahydrofuran. After 24 hours the reduced product was isolated in the usual way and hydrolyzed with hot



(92° C) dilute hydrochloric acid (2 *N*, 10 ml) for 6 hours. The resultant sugar had  $R_G$  0.85 (solvent A) and was indistinguishable from 2,3,4-tri-*O*-methyl-D-glucose,  $[\alpha]_D^{65}$  (c, 1.0) (Found: OMe, 41.5%. Calc. for  $C_6H_{18}O_6$ : OMe, 41.9%). When the sugar was dissolved in ethanol containing aniline and the mixture heated under reflux for 5 hours 2,3,4-tri-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. and mixed m.p. 145° C, was produced.

#### *Methylation of the Degraded Polysaccharide*

The polysaccharide (5 g) was acetylated using the conditions described above for the acetylation of the original polysaccharide. The acetylated product (7 g) was methylated with sodium hydroxide and dimethyl sulphate in the usual manner and the methylated product was isolated. This material still contained hydroxyl groups (infrared spectrum) and methylation was therefore completed by the method of Kuhn *et al.* (22). The product (3 g) had OMe, 42.5%, and its infrared spectrum showed a trace of hydroxyl band.

*Fractionation.*—The acidic methylated degraded gum was treated with diazomethane and the neutral product was extracted with chloroform–light petroleum mixture (b.p. 100–120° C) of increasing chloroform concentration. Two main fractions were obtained which had  $[\alpha]_D -50^\circ \pm 1^\circ$  (c, 1.0, acetone); OMe, 44%; and equiv. wt., 940.

#### *Hydrolysis of the Methylated Degraded Gum*

The methylated degraded gum (2.9 g) was hydrolyzed with hot 50% aqueous formic acid as described for the hydrolysis of the original methylated polysaccharide. The sugars (2.9 g) were separated into neutral (2.2 g) and acidic (0.61 g) fractions on ion-exchange columns. A quantitative analysis of the mixture by the method of Hirst, Hough, and Jones (10) and by weighing the fractions eluted from the cellulose chromatographic columns (see below) gave an approximate ratio of end group:tri-*O*-methyl-hexose:di-*O*-methyl-hexose of 1:2:1 (for fuller details see theoretical section).

#### *Fractionation of Neutral Sugars*

The neutral sugars (2.2 g) were fractionated on a cellulose column by the method of Hough, Jones, and Wadman (23). Six fractions were obtained. Fraction I (120 mg) had  $[\alpha]_D -30^\circ$  (c, 1.0) and was chromatographically identical in solvents A, B, and C with 2,3,5-tri-*O*-methyl-L-arabinose. Demethylation of a portion of the product with aqueous hydrobromic acid indicated the presence of arabinose only. A sample of the sugar was oxidized to the acid, the derived amide had a melting point of 134° C,  $[\alpha]_D -15^\circ$  (c, 1.0) and was indistinguishable from 2,3,5-tri-*O*-methyl-L-arabonamide. Fraction II (180 mg) was chromatographically pure and identical with 2,3,4,6-tetra-*O*-methyl-D-galactose. It had  $R_G$  0.88 (solvent A)  $[\alpha]_D +82^\circ$  (c, 1.0) and the derived 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-galactosylamine had a melting point of 190–191° C, not depressed on admixture with an authentic specimen, and  $[\alpha]_D +40^\circ$  (c, 1.0 in acetone; equilibrium value). Fraction III (130 mg) was a mixture of 2,3,4,6-tetra-*O*-methyl-D-galactose (30 mg) and an unknown sugar (100 mg). Fraction IV (500 mg) was chromatographically pure and was identified as 2,4,6-tri-*O*-methyl-D-galactose with  $R_G$  0.71 (solvent A), and  $[\alpha]_D +87^\circ$  (c, 1.0). The *N*-phenylglycosylamine derivative had a melting point of 171° C and  $[\alpha]_D 40^\circ$  (c, 1.0, acetone) and was indistinguishable by infrared spectroscopy from an authentic specimen. Fraction V (700 mg) was a mixture of 2,4,6-tri-*O*-methyl-D-galactose and of the 2,4-di-*O*-methyl derivative. Fraction VI (570 mg) had  $[\alpha]_D +80^\circ$  and crystallized. It was recrystallized from acetone and was identified as 2,4-di-*O*-methyl-D-galactose, m.p. 102° C,  $[\alpha]_D +86^\circ$  (c, 1.0), which was further characterized as the aniline derivative of melting point 215° C.

*Characterization of the Acidic Fraction*

The acidic fraction (0.61) moved as one material on the chromatogram and had  $[\alpha]_D +40^\circ$  ( $c$ , 1.0). It was not affected by hot dilute hydrochloric acid and therefore did not contain any oligosaccharide derivatives. It was converted by boiling its solution in methanolic hydrogen chloride to the corresponding ester  $\alpha$ - $\beta$ -glycoside. When this syrupy ester was dissolved in methanol and the solution was saturated with ammonia, the crystalline amides were produced. Recrystallization from ethanol-ether yielded pure 2,3,4-tri-*O*-methyl methyl  $\alpha$ -D-glucuronamide, which had a melting point of  $183^\circ\text{C}$  and  $[\alpha]_D +138^\circ$  ( $c$ , 1.0) (7).

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# SHEAR DEPENDENCE IN THE VISCOMETRY OF HIGH POLYMER SOLUTIONS

## A NEW VARIABLE-SHEAR CAPILLARY VISCOMETER<sup>1</sup>

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### ABSTRACT

The principles of capillary viscometry are reviewed, and design criteria for capillary viscometers to be used with non-Newtonian liquids are discussed. A description is given of a new type of variable-shear capillary viscometer—a modification of the Ubbelohde suspended-level viscometer—designed for measurements in the low-shear range. The instrument is rugged, convenient, and precise, and makes possible measurements at free fall over a 10-fold range of shear stress (or shear rate), a range that can easily be extended by use of two or more suitably modified instruments or by the application of external pressure. Experimental evidence is presented to show that proper choice of the dimensions of the instrument eliminates or minimizes most of the "effects" that limit the precision of measurements of relative viscosity (and related functions) of high polymer solutions in the range of low shear stresses.

### A. INTRODUCTION

For many years now the measurement of viscosity has been a powerful and much-used procedure in the study of high polymer systems and particularly of polymers in dilute solutions. In most of these studies, capillary viscometers have been used, because they are relatively inexpensive and convenient. Many different types of capillary viscometers have been designed to meet special needs. One particularly convenient viscometer (1), a modification of the Ubbelohde instrument (2), makes possible dilution in the viscometer itself and so greatly facilitates obtaining the data necessary for the determination of intrinsic viscosities (limiting viscosity numbers).

The ordinary capillary viscometers (Ostwald, Cannon-Fenske, Ubbelohde, etc.), when used as they were meant to be used, provide measurements all made at the same (or very nearly the same) driving pressure. They were not designed for use with non-Newtonian liquids, with which measurements should be made at a number of different driving pressures. Until fairly recently this seldom mattered. Now, however, there is more and more interest in polymers whose solutions are non-Newtonian liquids. For these, the familiar instruments and the time-honored procedures are not satisfactory and, unless suitably modified, may yield completely spurious results.

Several capillary viscometers that have been designed for use with non-Newtonian systems have been described (3, 4, 5, 6, 7). These give good results at relatively large shear stresses, say in the range 5–20 dynes/cm<sup>2</sup>. But most of them are not satisfactory for use at low stresses and hence cannot provide the data for a reliable extrapolation to zero shear stress. This is a serious inadequacy, for it is generally accepted that, in the study of polymers whose dilute solutions are non-Newtonian (polymers of very high molecular weight or with very stiff molecules), the quantity of greatest interest is the intrinsic viscosity at zero shear stress, a quantity that must be determined by extrapolation of data obtained at low shear stresses. That there is need for a rethinking of designs and procedures is evidenced by the fact that careful measurements with different variable-shear capillary viscometers have given results in the low-shear region that are

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at variance both with theory and with other experiments. Theory (8, 9) required a quadratic dependence on the shear stress to account for the fact that the viscosity of a liquid does not depend on the direction of the flow, that is, on the sign of the shear stress; and results obtained with Couette-type viscometers, which are intrinsically much better suited to shear-dependence studies, did in fact show this quadratic dependence (10), rather than a linear or exponential dependence indicated by results obtained with capillary viscometers (11, 12).

Since, in our judgment, existing variable-shear viscometers were either unsuited to, or inconvenient for, making precise, reliable measurements in the desirable range of low shear stresses, we have carefully reviewed the theoretical and experimental basis of capillary viscometry with a view to designing a suitable variable-shear capillary viscometer. As a result, we have developed a viscometer that has proved its worth during 3 years of use.

In this paper, we describe the new viscometer and discuss briefly the considerations which governed its design.

## B. DESIGNING THE VISCOMETER

### I. The Requirements

Ideally the viscometer should meet the following requirements:

- (a) It should be rugged and compact.
- (b) It should be simple and convenient to use. For example, it should not readily "clog"; it should be easy to load; it should permit dilution of the polymer solution in the instrument itself; and the flow times should not be excessively long.
- (c) It should yield precise data. The flow times should not be too short, and the driving pressure should be reproducible and steady.
- (d) It should make possible measurements at a number of different shear stresses in the low-stress range.
- (e) Its dimensions should be such that the kinetic energy effect, the drainage effect, and the effects of surface tension will be negligible at all shear stresses (or at least can be readily corrected for).

### II. The Poiseuille Equation and its Application

In designing an instrument to meet the requirements listed above, it is necessary to consider the Poiseuille equation (the basis of capillary viscometry) and reasons for deviations from it, and, in particular, the effects on these deviations of changes in concentration and in the shear stress.

The familiar form of the Poiseuille equation is

$$[1] \quad \eta = \frac{\pi R^4 p}{8VL} \cdot t$$

where  $R$  is the radius of the capillary and  $L$  is its length (cm),  $V$  is the volume (cm<sup>3</sup>) of liquid flowing through the capillary in time  $t$  (sec), and  $p$  is the driving pressure (dynes/cm<sup>2</sup>). In a viscometer in which the liquid flows under its own head,  $h$  (cm), the driving pressure is related to the head by the equation  $p = \bar{h}gd$ , where  $d$  is the density of the liquid. Then

$$[2] \quad \eta = \frac{\pi R^4 \bar{h}gd}{8VL} \cdot t$$

In deriving this equation, certain assumptions are made.

- (a) The flow is laminar.
- (b) There is no slip at the wall of the capillary, that is, the velocity of flow at the wall is zero. (For stresses less than  $10^2$  dynes/cm<sup>2</sup> this assumption seems to be valid (39).)
- (c) The liquid is incompressible.
- (d) All the energy applied to the liquid is used to overcome viscous resistance and is dissipated as heat (none, for example, being used to start the liquid flowing (no "yield value"), or to overcome effects due to surface tension, or to impart kinetic energy to the liquid).

This last assumption is never strictly valid. There is always a "kinetic energy effect" more or less large. When allowance is made for this, the Poiseuille equation becomes

$$[3] \quad \eta = \frac{\pi R^4 \bar{h} g d}{8 V L} \cdot t - \frac{m V}{8 \pi L} d \cdot \frac{1}{t}$$

where  $m$  is a semiempirical constant whose value depends on the shape of the capillary ends and on the velocity of flow (13, 14, 15). Because of this uncertainty in the value of  $m$ , the kinetic energy correction must be determined by calibration or, much better, made negligible by appropriate choice of the dimensional parameters. (It may easily be shown that the kinetic energy correction, expressed as a percentage correction, is proportional to  $R^4$ ,  $\bar{h}$ , and  $1/L^2$ ). If, then, the viscometer is appropriately designed, the simple Poiseuille equation [2] may be used in calculations.

In polymer-solution studies, the quantity desired is the viscosity ratio  $\eta/\eta_0$  (the ratio of the solution viscosity to the solvent viscosity) rather than the viscosity of the solution. The assumption is usually made that  $\eta/\eta_0 = t/t_0$ . This assumption really involves four assumptions:

- (a) that Poiseuille's equation [1] applies to both solution and solvent;
- (b) that the kinetic energy correction is negligible;
- (c) that the density ratio  $d/d_0$  differs negligibly from unity; and
- (d) that the quantity

$$\frac{\pi R^4 \bar{h} g}{8 V L},$$

collectively called the apparatus constant  $A$ , is really a constant,  $R$ ,  $\bar{h}$ ,  $V$ , and  $L$  having the same value for different pure liquids and solutions.

The first of these assumptions is valid for Newtonian liquids; but if the solution is non-Newtonian, the equation applies only under conditions such that the deviations from Newtonian behavior are slight (16, 17).

The second assumption we have already discussed.

The error involved in making the third assumption can be calculated (18) or can be determined by density measurements (19).

But what of the fourth assumption, that the parameters  $R$ ,  $\bar{h}$ ,  $V$ , and  $L$  in the apparatus constant are truly constant? Let us consider each of these parameters in turn.

#### *The Radius of the Capillary, $R$*

The radius of the capillary may be altered in changing from solvent to solution if polymer is absorbed on the capillary wall. The effective radius  $R^*$  then would be

$$R^* = R - a$$



where  $a$  is the thickness of the absorbed layer.<sup>3</sup> Öhrn (22) has obtained evidence of such a reduction in radius. It leads to an apparent viscosity ratio,  $\eta_r^*$ , that is greater than the true ratio,  $\eta_r$ . According to Öhrn

$$\eta_r = \eta_r^* \left( 1 - \frac{4a}{R} \right).$$

From this it follows that

$$[4] \quad \frac{\eta_r - 1}{c} = \frac{\eta_r^* - 1}{c} - \frac{4a}{R} \cdot \frac{\eta_r^*}{c}$$

and that the "absorption" error, expressed as a percentage of the true reduced viscosity, amounts to

$$\frac{4a}{R} \cdot \frac{\eta_r^*}{(\eta_r^* - 1)} \cdot 100.$$

Even at  $\eta_r = 1.2$ , the error in  $(\eta_{sp})/c$  is still 1.2% assuming that the thickness of the absorbed layer is 1250 Å (which is about what Öhrn found it to be) and that the radius of the capillary is 0.0250 cm. Since the error in  $(\eta_{sp})/c$  is larger the lower the concentration of the solution, the slope of the  $(\eta_{sp})/c$  versus  $c$  line will be greater when corrected values of  $(\eta_{sp})/c$  are plotted than when uncorrected values are plotted.<sup>4</sup> Hence the true value of  $[\eta]$  will be smaller than that obtained if corrections are not made. This suggests that in the determination of  $[\eta]$  by extrapolation, greater weight should be given to the points at higher concentrations than to those where  $\eta_r$  approaches 1.2. It is, however, worth mentioning that if the desorption of the polymer layer is slow (24), the error due to absorption will be smaller if the measurements are made with progressively more dilute solutions (as they are when dilution is made in the bulb of the viscometer) and if the flow time of solvent is measured after rather than before the flow times of the solutions are measured.

#### *The Hydrostatic Head, $\bar{h}$*

In any capillary viscometer, the hydrostatic head decreases during flow. Therefore a mean head must be used in calculations. What this mean head is depends upon the shape of the efflux bulb, and on whether the liquid flows out of the capillary into the air as in the Ubbelohde suspended-level viscometer or into another vessel, as in an Ostwald-type viscometer. In a Ubbelohde viscometer<sup>5</sup> in which the efflux bulb is spherical and in which there is negligible kinetic energy effect, the true mean head  $\bar{h}$  for discharge into air is given by the expression (26)

$$[5] \quad \bar{h} = \frac{4/3R_b}{2c - (c^2 - 1) \ln \frac{c+1}{c-1}}$$

<sup>3</sup>Actually an apparent reduction in radius of this form may be due in part or whole to other effects such as the "size effect" encountered with suspensions of rigid particles (20) and the hydrodynamic repulsion by the wall which increases with the velocity of flow (21). Regardless of the cause, the observed apparent reduction in radius is of the order of magnitude of a particle radius.

<sup>4</sup>It may be shown (23) that the error in the slope, expressed as a percentage error, is equal to

$$\frac{400a/R}{k'[\eta]^2 c^2}.$$

For example, with our polystyrene fraction  $T_8$ , for which  $[\eta] = 9.32$  dl/g and  $k' = 0.31$  the percentage error would be 1.87% at a concentration,  $c$ , of 0.063 g per 100 ml (at which  $\eta_r = 1.8$ ) and 7.2% at a concentration of 0.032 g per 100 ml (at which  $\eta_r = 1.3$ ). To keep this error reasonably small, the measurements should be made at concentrations such that  $\eta_r$  is not less than about 1.5 (or else an absorption correction should be made).

<sup>5</sup>The calculation of the mean head in an Ostwald-type viscometer is more complicated. It is discussed in a recent paper by Overbeek (26).

where  $R_b$  is the radius of the bulb and  $c = h_m/R_b$  and  $h_m$  is the algebraic mean of the initial and final heads (provided that the fiducial marks are equidistant from the spherical bulb). After expansion of the logarithmic term this reduces to

$$[6a] \quad \bar{h} = \frac{h_m}{1.0200 \frac{1}{c^2} + 0.086 \frac{1}{c^4}}$$

or, for all practicable heads,

$$[6b] \quad \bar{h} = h_m.$$

Expression [5] is not strictly valid for non-Newtonian liquids (27). Nevertheless, the deviation from it is negligibly small, much smaller, say, than the error due to kinetic energy effect, even in a well-designed viscometer.

There is, however, an effect on the hydrostatic head which may not be negligible, namely, that due to *surface tension*. With organic solvents and their solutions the effect is very small in the usual capillary viscometers ( $h \sim 10$  cm); but in viscometers with very low heads ( $h < 3$  cm), and with the smaller bulb that must be used at these low heads to give a convenient flow time, the effect becomes very significant. Indeed with water and with aqueous solutions, it can amount to 30% or more of the mean head. Accordingly, a variable-shear viscometer for use at low shear stress should be so designed that surface tension effects are effectively eliminated or, failing that, can be corrected for with as little inconvenience as possible.

In various viscometers that have been designed for use at low shears, attempts have been made to eliminate the surface tension effect by having the effect of surface tension at the advancing meniscus exactly offset that at the receding (or falling) meniscus (see, for example, Sprokel's design for an Ostwald viscometer (28), Golub's work with a simple U-tube viscometer (11), and Signer and Berneis' work with an inclined capillary (5)). In all of these, however, one meniscus is advancing onto a dry surface and the other is receding from a wet surface. This gives rise to a hysteresis effect which manifests itself as an apparent yield value (29). This effect is the more serious the lower the hydrostatic head. In other words, it is most serious just where reliable data are most desired.

The viscometer in which the surface tension can best be coped with is the Ubbelohde, or suspended-level, viscometer. In this there is only one moving meniscus—the falling one. The other one is kept stationary and given a fixed radius of curvature, at the suspended level. The radius of curvature of the inverted surface can be selected so that surface tension exerts a downward pull at the suspended level that exactly counterbalances the upward pull at the falling meniscus. The required radius of curvature is calculated from the relation

$$[7] \quad R_0 = \frac{2\gamma}{d} \cdot \frac{1}{\langle h_r \rangle}$$

where  $\gamma$  is the surface tension and  $\langle h_r \rangle$  is the "volume average" capillary rise in the bulb and the tubing between the fiducial marks. Values of the quantity  $\langle h_r \rangle$  can be calculated (30, 13, 31) from the expression

$$[8] \quad \langle h_r \rangle = \frac{\sum \langle h_i \rangle_r \Delta V_i}{\sum \Delta V_i}$$

where  $\sum \Delta V_i$  is the total volume of the bulb, including the volume of tubing between the marks.

Contrary to Ubbelohde's claim, a value of  $R_0$  calculated for a given liquid does not apply for every other liquid; it applies only when that liquid, or another liquid for which the ratio  $\gamma/d$  has the same value, is used in the viscometer. Fortunately many of the common organic solvents do have nearly the same surface tension - density ratio, namely, about 30 dynes  $\text{cm}^2 \text{g}^{-1}$  (see Table I). Fortunately, too, a dilute polymer solution

TABLE I  
Surface tension-density ratios (25° C)  
(Data obtained from (32) and (33))

Solvent	$\gamma$ , dynes/cm	$d$ , g/cm <sup>3</sup>	$\gamma/d$ , dynes $\text{cm}^2/\text{g}$
Toluene	27.20	0.862	31.5
Benzene	27.47	0.874	31.4
Cyclohexane*	23.82	0.769	31.0
Methyl ethyl ketone	24.0	0.799	30.0
Acetone†	23.32	0.791	29.5
Carbon tetrachloride	26.15	1.58	16.5
Water	72.0	0.997	72.2

\*At 36° C. †At 20° C.

in an organic solvent has very nearly the same value of the  $\gamma/d$  ratio as the solvent itself. So a viscometer designed for use with one organic solvent and its solutions is suitable for use with most others. It is *not*, however, suitable for use with water, for which  $\gamma/d = 72.2$  dynes  $\text{cm}^2 \text{g}^{-1}$ , or for aqueous solutions.

#### *The Efflux Volume, V*

The actual volume of the efflux bulb does not necessarily equal the efflux volume  $V$ , the volume of liquid that passes through the capillary in flow. The true efflux volume will be the volume of the bulb (the volume between the fiducial marks) less the volume  $V_d$  of liquid left adhering to the walls. This volume, the *drainage correction* in the efflux volume, varies directly as the viscosity of the liquid and inversely as its flow time. It is, therefore, independent of the liquid *provided that the liquid flows under its own head* (34). Hence a drainage correction in the viscosity ratio (and derived functions) is not necessary if all measurements are made at free fall; it is necessary, however, if external pressures are used to vary the shear stress (27).

#### *The Capillary Length, L*

The effective length of the capillary  $L$  is not identical with the actual length of the capillary  $L_0$ , but is greater than it by the quantity  $nR$ , where  $R$  is the radius of the capillary and  $n$  is a parameter whose value is about 0.566. When a capillary of length  $L$  is divided into two sections, as in our viscometer, the end correction would be doubled, becoming  $2nR$ . The value of  $n$  may vary slightly with driving pressure, but in any event the end correction may be made negligible by making  $L$  large enough. (For viscoelastic liquids there is another "end correction" related to the "recoverable shear",  $S_R$  (35). Taking this into account, the total end correction in our viscometer amounts to  $2(n + S_R/2)R$ , where  $S_R = 0$  for Newtonian liquids,  $S_R \sim 1$  for most polymer solutions, and  $S_R \sim 10$ -100 for highly viscoelastic liquids such as molten polyethylene and aluminum soap solutions.)

### *III. The Design*

The viscometer, Fig. 1, was designed taking all these factors into consideration. Some features of it need comment.

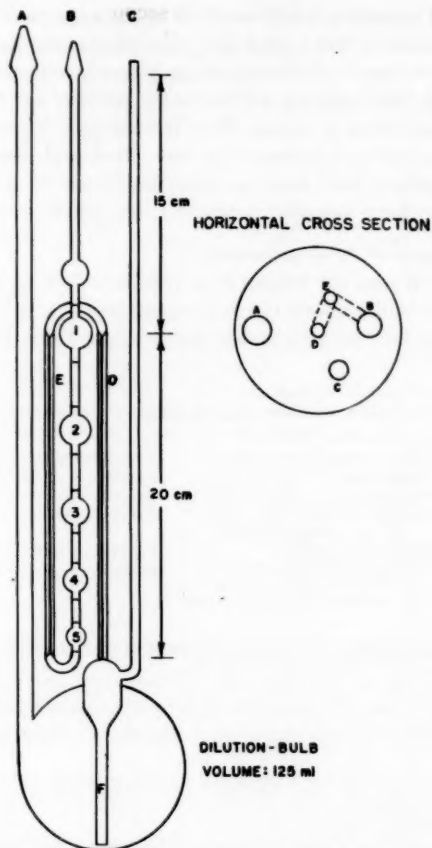


FIG. 1. Modified Ubbelohde variable-shear viscometer: (A) filling tube, O.D. 1 cm; (B) bulb system; (C) air inlet tube, O.D. 0.6 cm; (F) O.D. 0.6 cm, I.D. 0.4 cm (F almost touches the bottom of dilution bulb).

(a) The viscometer is provided with five efflux bulbs, each with its own pair of fiducial marks. With these can be achieved five different accurately reproducible mean heads, corresponding to shear stresses varying over a 10-fold range. Since the heads are built into the instrument, drainage corrections are unnecessary (so long as external pressure is not applied)

(b) The viscometer is of the Ubbelohde type, to facilitate elimination or correction of surface tension effects. The radius of curvature of the hemispherical suspended level is such that there is no surface tension effect at the lowest head when toluene is the solvent. (This means an overcorrection for the other bulbs, but the resulting negative corrections are very small in the next higher head and small even at the highest head. The *relative* error is always negligible with toluene as solvent and indeed with the other organic solvents of Table I for which  $\gamma/d \approx 30$ .)

(c) The viscometer is modified so that dilution of the solution can be accomplished without removing the solution from the instrument. This is possible because the position

of the second meniscus is independent of the volume of liquid in the viscometer. Incidentally, this feature of the Ubbelohde also eliminates loading errors.

(d) Precision-bore capillary tubing is used, and with no bends in it, to ensure that liquid flow in the capillary will be truly laminar (at the driving pressures used).

(e) A lowest head of about 2 cm is achieved, in conjunction with the long length of capillary required to minimize the end effect and kinetic energy effect, by dividing the length of capillary tube into two lengths joined by a wider-bore U tube. With the two lengths of capillary disposed vertically, the whole instrument is compact and rugged.

#### IV. Dimensions of the Viscometer

The radius  $R$  and the length  $L$  of capillary tubing, the volumes of the bulbs, and the heights of the bulbs above the suspended level (which of course govern the heads) were chosen after balancing all relevant factors (see Table II). Two viscometers were designed

TABLE II  
Considerations affecting the choice of dimensional parameters  $R$ ,  $L$ ,  $V$ , and  $h$

Shear stress, dynes/cm <sup>2</sup>	Proportional to	$R$ ,	$L^{-1}$ ,	$h$
Flow time, $t$	Proportional to	$R^{-4}$ ,	$L$ ,	$h^{-1}$
Kinetic energy effect (%)	Proportional to	$R^4$ ,	$L^{-2}$	$V$
Surface tension effect (%) (if not compensated for)	Proportional to			$V_b^{-1/3}$ , $h^{-1}$
End effect (%)	Proportional to	$R$ ,	$L^{-1}$	
Absorption effect (%)	Proportional to	$R^{-1}$		

\*For spherical bulbs of dry volume  $V_b$ .

to provide two different, and overlapping, shear-stress ranges.

The specifications for the two viscometers are listed in Tables III and IV. (The viscometers themselves, as fabricated by the master glassblower of Canadian Laboratory Supplies, Montreal, conformed very closely to these specifications.)

### C. EVALUATION OF THE VISCOMETER

#### I. Experimental Tests

A simple and direct test is to compare measured flow-time ratios with kinematic viscosity ratios, for two different liquids. The Poiseuille equation [3] may be written in the form

$$[9] \quad \nu = \frac{\pi R^4 h g}{8 V L} \cdot t - \frac{m V}{8 \pi L} \frac{1}{t} = A t - B \frac{1}{t}$$

where  $\nu$  is the kinematic viscosity  $\eta/d$ . If the kinetic energy term is negligible, this reduces to

$$[10] \quad \nu = \frac{\pi R^4 h g}{8 V L} \cdot t = A t.$$

If  $A$  is constant, the ratio of flow time for two different liquids should be the ratio of their kinematic viscosities. Furthermore, if the two liquids are Newtonian, this ratio should be the same at all shear stresses.

Such a comparison was made for several pairs of liquids in two viscometers, IIA-1 and IIB-1, made to the specifications of Tables III and IV, respectively. The results of one comparison, using benzene<sup>6</sup> and toluene,<sup>6</sup> are given in Table V.

<sup>6</sup>The solvents used in the experiments discussed in this paper were carefully purified in the manner already described (36).



TABLE III  
Specifications for viscometer IIA (organic solvents)  
(Shear stress range, 0.5–4 dynes/cm<sup>2</sup>)

Radius, $R$ , of capillary	0.025 cm (precision bore)				
Length, $L$ , of capillary (2×25.0 cm)	50.0 cm				
Radius of curvature, $R_0$ , of hemisphere	0.33 cm				
Bulbs (spherical)	1	2	3	4	5
Head $h_m$ (cm)	20	15	10	5	2
Volume $V$ (cm <sup>3</sup> )	1.50	1.12	0.75	0.40	0.30
Flow time (sec) for benzene	171	170	171	183	345
Kinetic energy correction (%)	0.11	0.08	0.06	0.03	0.01

TABLE IV  
Specifications for viscometer IIB (organic solvents)  
(Shear stress range, 1.5–11 dynes/cm<sup>2</sup>)

Radius, $R$ , of capillary	0.025 cm (precision bore)				
Length, $L$ , of capillary (2×15)	30.0 cm				
Radius of curvature, $R_0$ , of hemisphere	0.413 cm				
Bulbs (spherical)	1	2	3	4	5
Head $h_m$ (cm)	30	20	15	9	4
Volume $V$ (cm <sup>3</sup> )	3.0	2.0	1.5	0.9	0.4
Flow time (sec) for benzene	137	137	137	137	137
Kinetic energy correction (%)	0.47	0.31	0.24	0.14	0.06

TABLE V  
Comparison of flow-time ratios and kinematic viscosity ratios for benzene and toluene at 20° C

Benzene	$\gamma/d = 31.4$ dynes cm <sup>2</sup> /g		$\nu_B = 0.738$ (c.s.t.)		$\nu_B/\nu_T = 1.092$	
Toluene	$\gamma/d = 31.5$ dynes cm <sup>2</sup> /g		$\nu_T = 0.676$ (c.s.t.)			
Viscometer IIA						
Bulb	1	2	3	4	5	
$t_B$ (sec)	147.99	148.27	147.20	161.48	294.78	
$t_T$ (sec)	135.44	135.78	134.43	147.72	269.78	
$t_B/t_T$	1.093	1.092	1.095	1.093	1.093	Av. 1.093
Viscometer IIB						
Bulb	1	2	3	4	5	
$t_B$	134.36	133.78	137.07	134.63	142.70	
$t_T$	123.08	122.44	125.48	123.16	130.87	
$t_B/t_T$	1.092	1.093	1.092	1.093	1.090	Av. 1.092

The constancy of the flow-time ratios, and the agreement with the kinematic viscosity ratio, indicate that both kinetic energy and surface tension effects are minor.

That the surface tension effect on  $t_r$  is negligible is indicated by the fact that the ratio has the same value at very low heads (bulb 5) as at heads 10 times greater (bulb 1).

This constancy, however, is not proof that the surface tension effect on  $h$ , and therefore on  $t$ , is negligible.

It may be shown that (with negligible kinetic energy effect)

$$\nu_r = t_r \left[ 1 - \frac{1}{\bar{h}} (\langle h_r \rangle_1 - \langle h_r \rangle_2) - \frac{1}{\bar{h}^2} (\langle h_r \rangle_1 \langle h_r \rangle_2 - \langle h_r \rangle_2^2) \right]$$

where  $\bar{h}$  is the mean head,  $\langle h_r \rangle_1$  is the correction in the head due to surface tension of liquid 1, and  $\langle h_r \rangle_2$  is the correction in the head due to surface tension of liquid 2. Since  $\langle h_r \rangle$  depends on  $\gamma/d$ , the surface tension–density ratio, it follows that (except for

hysteresis effects which are eliminated in an Ubbelohde-type viscometer) the surface tension effect in the *ratio* of the kinematic viscosities will be nil if the two liquids have the identical  $\gamma/d$  ratios, and will be negligible except when  $\gamma/d$  ratios differ appreciably.

This means that the effect of surface tension in  $t_r$  or  $\eta_r$  (or other relative functions like  $(\eta_{sp})/c$  or  $[\eta]$ ) can be neglected with most organic solvents and their solutions even when there is an appreciable surface tension effect in  $h$ . It does *not* mean, however, that *all* surface tension effects can be neglected. There can be a very significant effect on the shear stress. With non-Newtonian liquids, for example, the shear stress  $\tau$  (or the shear rate  $D$ ) is a very significant variable. It is calculated from the mean head  $\bar{h}$ . But a calculation of the mean head in flow from measured values of  $h_{\text{initial}}$  and  $h_{\text{final}}$  using equation [5] (or its simplified forms [6a] or [6b]) does not take into account the capillary rise in the bulb and, hence, yields a mean head which is in error (the relative error being greater the smaller  $\bar{h}$  is). At low heads the percentage error in  $\bar{h}$ , and therefore in  $\tau$  or  $D$ , can be very large. On the other hand, with a viscometer such as ours, the  $\bar{h}$ 's whose direct measurement would lead to greatest error, the small heads, can be determined indirectly. Since

$$\bar{h} = \frac{\eta}{d} \frac{8VL}{\pi R^4 g} \cdot \frac{1}{t},$$

measurements at the large values of  $\bar{h}$  (when surface tension effects are negligible) with a liquid of known  $\eta/d$ , give a measure of  $8L/g\pi R^4$  which, combined with measurements of  $V$  and  $t$  at the low heads, make it possible to calculate  $\bar{h}$ .

That the kinetic energy effects are small in these viscometers is also indicated by the constancy of the flow-time ratios. The kinetic energy effect on  $t_{\text{benzene}}/t_{\text{toluene}}$  should be *relatively* larger in bulb 1 than in bulbs 5 or 4; but within the limits of error no difference in the ratio, as measured with bulb 1 and with bulbs 5 or 4, is detectable. But this is not surprising. If the percentage kinetic energy effect is small in a flow time, and we designed the viscometer to make it so, it will be much smaller still in a flow-time ratio. In other words, the test is not a very sensitive one.

A second and more sensitive test of the extent to which unwanted effects have been reduced involves the determination of the constants  $A$  and  $B$  in the modified viscosity equation [9]. These can be evaluated, as suggested by Higgins (37), from a plot of  $v/t$  versus  $1/t^2$ ;  $A$  is then the intercept and  $B$  is the slope constant. For this evaluation, we measured the flow times of benzene at 20° and 40° and toluene at 20°, 40°, and 60° C and we obtained the corresponding kinematic viscosities from Timmermans (32). Values of  $A$  and  $B$  obtained from the plots are given in Table VI.

TABLE VI  
Calibration constants for the two viscometers

Bulb	IIA			IIB		
	$A \times 10^{-5}$	$B \times 10^{-2}$	% Kinetic energy correction*	$A \times 10^{-5}$	$B \times 10^{-2}$	% Kinetic energy correction*
1	5.02	0.621	.31	5.55	1.196	.66
2	5.01	0.516	.26	5.56	0.929	.52
3	5.02	0.101	.05	5.42	0.752	.41
4	4.50	0.094	.04	5.50	0.520	.29
5	2.50	0.093	.02	5.14	0.066	.03

\*Calculated for a liquid for which  $\nu = 10^{-2}$  stokes.

From the values of  $A$  and  $B$ , the percentage kinetic energy correction in the flow time,  $AB/v^2$ , can be readily calculated. In Table VI are listed the corrections for benzene at 20° C. Considering the difficulty of fabricating an instrument like this exactly to specifications, these agree remarkably well with those calculated in Tables III and IV.

From our value of  $A$  and  $B$  and our measured values of  $t$ , we calculated kinematic viscosities of toluene at 20°, 40°, and 60°. These are given in Table VII.

TABLE VII  
Kinematic viscosities of toluene at 20°, 40°, and 60° C  
(calculated as  $At$  and as  $At-B/t$  (in c.s.t.))

Bulb	20° C		40° C		60° C	
	$v = At$	$v = At-B/t$	$v = At$	$v = At-B/t$	$v = At$	$v = At-B/t$
Viscometer II-A-1						
1	.681	.676	.553	.547	.465	.459
2	.680	.676	.552	.548	.464	.458
3	.689	.675	.549	.546	.463	.458
4	.677	.676	.546	.546	.460	.459
5	.673	.673	.540	.540	.455	.455
Viscometer II-B-1						
1	.648	.674	.557	.545	.469	.454
2	.681	.674	.553	.544	.465	.454
3	.680	.674	.550	.543	.463	.454
4	.677	.673	.546	.541	.460	.454
5	.673	.673	.544	.543	.454	.454
Average		.674		.544		.456

From these data it is clear that the kinetic energy corrections are small but still significant, in the kinematic viscosities. In a flow-time ratio they would be very small. Even in a specific viscosity  $\eta_{sp}$  or intrinsic viscosity  $[\eta]$  the corrections would, in the usual range  $\eta_r = 1.1-1.9$ , always be less than 1% and in the lower three bulbs less than 0.1%.

The kinematic viscosities measured at widely different heads are identical within experimental error. This fact is not, in itself, proof that the surface tension effects have been eliminated in these viscometers, for the apparatus constant  $A$  for each bulb was obtained by calibration. It is possible, however, to calculate from the calibration values of  $A$  the effective mean hydrostatic head corresponding to each bulb. If the surface tension effect has been eliminated, these effective mean heads should be the same as the mean heads calculated from measured initial and final heads ( $\bar{h} = h_m$ ). The appropriate measurements and calculations were made, and the results for viscometer II-A-1 are assembled in Table VIII.

TABLE VIII  
Comparison of mean heads calculated from  
apparatus constant  $A$  and from measured heads

Bulb	$\bar{h}_{calc}$ (cm)	$h_m$ (cm)
Viscometer II-A-1		
1	20.57	20.53
2	15.47	15.52
3	10.43	10.38
4	5.23	5.17
5	2.16	2.17

The agreement between the measured mean head  $h_m$  and the calculated mean head  $h_{calc}$  is convincing evidence that the effect of surface tension on the mean head has been eliminated.

In summary, these and other similar calibration data show that the viscometers do indeed measure viscosities precisely, and over a wide range of shear stresses.

The measurements so far discussed have been made with pure solvents. Over the past 3 years, these, and other viscometers made to the same design, have been used in several different investigations, and all have proved to be very satisfactory both in routine measurements and for research purposes. They are easy to use and to clean and they are capable of giving precise data even at shear rates as low as  $40 \text{ sec}^{-1}$ .

The data obtained in these investigations will be given and discussed elsewhere. Here, it is probably sufficient to provide one example. Measurements were made with solutions, in toluene, of a polystyrene of very high molecular weight. For preparation of the solutions and purification of the solvent, see reference 36. The measurements were made at different concentrations to permit extrapolation to zero concentration at all the shear stresses obtainable at free fall in the two viscometers II-A-1 and II-B-1. The measured flow times for the solutions, which were markedly non-Newtonian, were used to calculate relative flow times ( $t/t_0$ ) and from these relative viscosities (at the maximum shear stress  $\tau_R$ , at the wall) were calculated according to the equation (38)

$$(\eta_r)_{\tau_R} = t_r [4 / (3 + d \log q_R / d \log \tau_R)].$$

From  $(\eta_r)_{\tau_R}$  the corresponding values of reduced specific viscosity  $(\eta_{sp}/c)_{\tau_R}$  were calculated and used to obtain the intrinsic viscosity at constant shear stress  $[\eta]_{\tau_R}$ . A typical plot of  $(\eta_{sp}/c)_{\tau_R}$  vs.  $c$  and of  $[\eta]_{\tau_R}$  vs.  $\tau_R$  is given in Figs. 2 and 3.

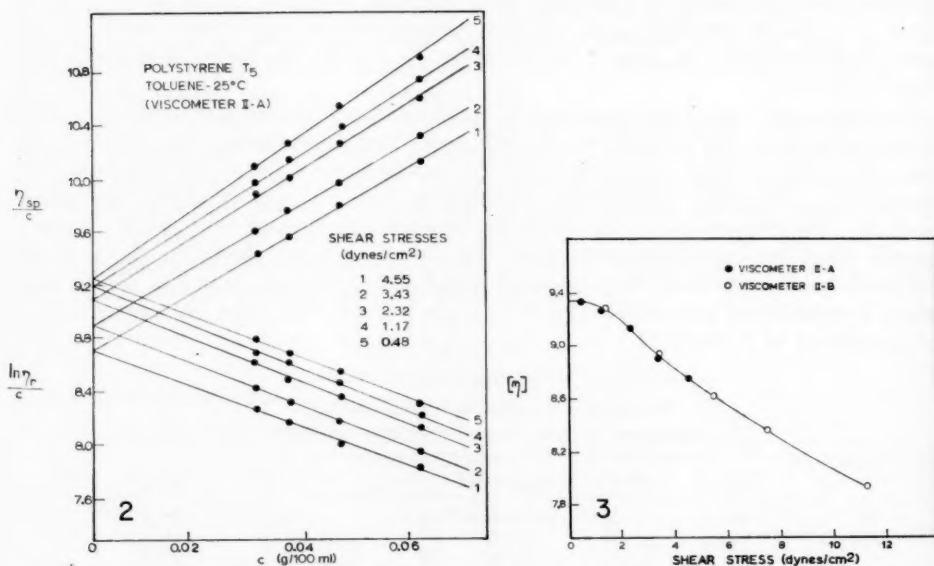


FIG. 2. A typical set of data obtained in the new variable-shear viscometer (reduced viscosities and inherent viscosities at five different shear stresses).

FIG. 3. Variation of intrinsic viscosity with shear stress for a polystyrene fraction of very high molecular weight,  $T_8$ . (Note the overlapping of the data obtained in the two different viscometers.)

The points obtained with the two viscometers fall satisfactorily on the same curve. The curve exhibits the expected levelling off at low shear stresses, a feature that makes extrapolation to zero stress simple and safe.

It is worth stressing that this levelling off can be, and probably has been in some other investigations, obscured by effects of hysteresis and surface tension already mentioned. For example, even though surface tension effects may almost cancel out in  $\eta_r$  (and, therefore, in  $\eta_{sp}/c$ ) they can still be significant in the shear stress  $\tau$  (or the shear rate  $D$ ), and being greater the lower the shear stress, they can be the cause of a spurious upcurve at very low shear stresses.

Our experience with these viscometers convinces us that they should be very useful both for determining whether or not a polymer-solvent system is non-Newtonian and for making measurements with it if it is. Further, the instruments are suitable both for making the low-shear measurements necessary for a reliable extrapolation to zero shear and for making determinations of viscosity functions at some arbitrary shear rate or shear stress.

#### ACKNOWLEDGMENTS

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# THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

## V. THE ANALYSIS OF DECEPTIVELY SIMPLE SPECTRA<sup>1</sup>

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### ABSTRACT

The analyses of the  $ABX$ ,  $A_2X_2$ , and  $ABXY$  types of spectra are discussed in detail under the conditions for which the observed spectra give less than the theoretical number of transitions. These conditions for which an observed spectrum is deceptively simple are derived from the general analyses, and experimental examples of such spectra are given.

The complete analyses of the more simple types of nuclear magnetic resonance spectra have been presented in the preceding papers of this series (1, 2, 3, 4). From these and other papers (8) it is seen that the problem of the analysis of any N.M.R. spectrum for which explicit energies and intensities can be formulated reduces to the problem of assigning the experimentally observed transitions. In some cases it is found that considerably fewer transitions are observed than one would expect from the theoretical spectra. This is due to the fact that some of the theoretical transitions nearly coalesce and others are very weak. In principle, higher resolution might reveal more lines but in practice many such spectra are encountered in which it is not possible to resolve the overlapping lines with presently available N.M.R. spectrometers. In these cases there may be more than one assignment and interpretation of the spectrum. In this paper some of the general analyses will be considered in detail for those cases for which this deceptively simple type of spectrum is obtained. In these cases it is found that the separation of the lines in each group of the spectrum becomes equal to the average of two or more of the coupling constants involved and explicit values for each of the coupling constants cannot be obtained from such spectra. The simplest system for which this type of spectrum can be obtained is the  $ABX$  system. This system will now be considered in some detail, as the behavior of the spectrum for more complex systems is very similar, although the calculations become more laborious.

### The $ABX$ System

The general  $ABX$  analysis has already been given by Bernstein, Pople, and Schneider (1). It is convenient to use the nomenclature of reference 1 with the additional definitions

$$\begin{aligned} L &= \frac{1}{2}(J_{AX} - J_{BX}), & \delta &= \sigma_B - \sigma_A, \\ [1] \quad N &= \frac{1}{2}(J_{AX} + J_{BX}). \end{aligned}$$

Parameters  $D$  and  $\phi$  are then defined from

$$\begin{aligned} [1a] \quad D_{\pm} \cos 2\phi_{\pm} &= \frac{1}{2}\eta H_0 \delta \pm (L/2), \\ D_{\pm} \sin 2\phi_{\pm} &= \frac{1}{2}J_{AB}. \end{aligned}$$

The transition energies and intensities for this system are given in terms of these quantities in Table I. This system in the general case gives the 12 transitions shown in Fig. 1(a)

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TABLE I  
Energies and intensities for ABX

Transition	Origin	Energy	Relative intensity
1	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-\frac{1}{2}N-\frac{1}{2}J_{AB}-D_-$	$1-\sin 2\phi_-$
2	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+\frac{1}{2}N-\frac{1}{2}J_{AB}-D_+$	$1-\sin 2\phi_+$
3	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-\frac{1}{2}N+\frac{1}{2}J_{AB}-D_-$	$1+\sin 2\phi_-$
4	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+\frac{1}{2}N+\frac{1}{2}J_{AB}-D_+$	$1+\sin 2\phi_+$
5	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-\frac{1}{2}N-\frac{1}{2}J_{AB}+D_-$	$1+\sin 2\phi_-$
6	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+\frac{1}{2}N-\frac{1}{2}J_{AB}+D_+$	$1+\sin 2\phi_+$
7	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-\frac{1}{2}N+\frac{1}{2}J_{AB}+D_-$	$1-\sin 2\phi_-$
8	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+\frac{1}{2}N+\frac{1}{2}J_{AB}+D_+$	$1-\sin 2\phi_+$
9	X	$\eta H_0(1-\sigma_X)-N$	1
10	X	$\eta H_0(1-\sigma_X)+D_+-D_-$	$\cos^2(\phi_+-\phi_-)$
11	X	$\eta H_0(1-\sigma_X)-D_++D_-$	$\cos^2(\phi_+-\phi_-)$
12	X	$\eta H_0(1-\sigma_X)+N$	1
13	Comb.	$\eta H_0(1+\sigma_X)$	0
14	Comb.	$\eta H_0(1-\sigma_X)-D_+-D_-$	$\sin^2(\phi_+-\phi_-)$
15	Comb.	$\eta H_0(1-\sigma_X)+D_++D_-$	$\sin^2(\phi_+-\phi_-)$

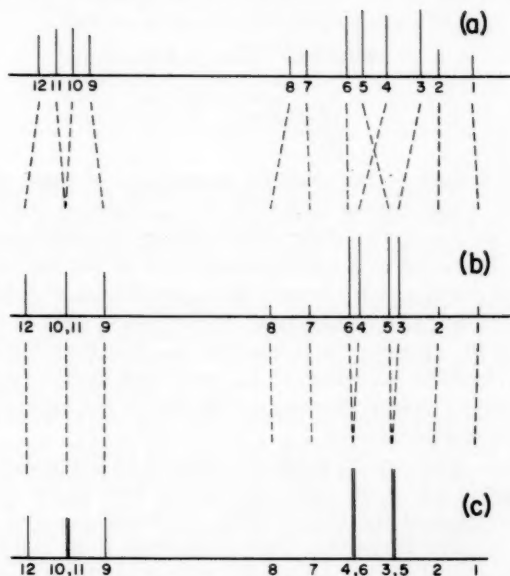


FIG. 1. Typical spectra of the ABX system when (a)  $\delta_{AB}$  is large compared to  $J_{AB}$ , (b)  $\delta_{AB}$  or  $L = 0$ , (c)  $\delta_{AB} = 0$  and  $L/J_{AB} \rightarrow 0$ .

(ignoring the weak combination lines which are rarely observed). However, the number of observable transitions can be reduced in certain cases, down to a minimum of five lines (e.g. Fig. 1(c)). The conditions necessary for the 12-line spectrum to simplify to the 5-line one can be found from Table I. First consider the spectrum when the chemical shift difference between nuclei A and B (i.e.  $\delta$ ) equals zero. In this case from eqs. [1a]

$$D_+ = D_- = \frac{1}{2}\{J_{AB}^2 + L^2\}^{\frac{1}{2}}$$

and

$$\sin 2\phi_{\pm} = \frac{J_{AB}}{2D_+} = \frac{J_{AB}}{2D_-} = \frac{J_{AB}}{2D}.$$

The  $X$  spectrum is now a triplet, transitions 10 and 11 having coalesced, but the  $AB$  portion will still be an 8-line spectrum (see Fig. 1(b)); thus the complete spectrum has 11 lines and the assignment is straightforward. A similar spectrum is obtained for the case when  $L = 0$ . However, by inspection of Table I, it can be seen that if  $\delta = 0$ , and also  $L$  is small compared with  $J_{AB}$ , i.e.  $2D \rightarrow J_{AB}$  and  $\sin 2\phi_{\pm} \rightarrow 1$ , then the intensities of transitions 1, 2, 7, and 8 will approach zero and the strong transitions 3 and 5, and 4 and 6 will coalesce (see Fig. 1(c)). The  $X$  spectrum remains a triplet, thus the total spectrum will now consist of only five lines. Also the separation between transitions (3, 5) and (4, 6) and between transitions 9, (10, 11), and 12 is constant and equal to  $N$ , i.e.  $\frac{1}{2}(J_{AX} + J_{BX})$ .

The conditions necessary for the 12-line spectrum to degenerate to a simple 5-line spectrum can now be derived directly from Table I. For this to occur, the separations between lines 3 and 5, 4 and 6, and 10 and 11 must all be less than the half-height width of the component lines ( $\Delta\nu_{\frac{1}{2}}$ ), and the intensities of lines 1, 2, 7, and 8 must all be less than a given fraction ( $i$ ) of the total intensity. These two sets of conditions are covered by the limits

$$[2] \quad (\eta H_0 \delta + L)^2 / 2J_{AB} < \Delta\nu_{\frac{1}{2}}$$

and

$$[3] \quad \frac{1}{2} \left( \frac{\eta H_0 \delta + L}{J_{AB}} \right)^2 < i$$

where here  $\eta H_0 \delta$  and  $L$  refer to the absolute magnitudes of these quantities. If  $J_{AB}$  is less than  $\Delta\nu_{\frac{1}{2}}/i$ , eq. [3] is the more general case, if  $J_{AB}$  is greater than  $\Delta\nu_{\frac{1}{2}}/i$ , eq. [2] must be used. The quantities  $\Delta\nu_{\frac{1}{2}}$  and  $i$  will be determined by the spectrometer used. For the Varian spectrometer operating at a radio frequency of 60 Mc/sec, the line width ( $\Delta\nu_{\frac{1}{2}}$ ) is about 0.3 c.p.s. and the sensitivity is such that a small peak of 1/50th of the intensity of a neighboring strong line can be observed. If the strong peak is taken as one of the  $AB$  lines, then  $i \approx 2/50$ . Thus eq. [3] is used for  $J_{AB}$  less than 8 c.p.s., eq. [2] for  $J_{AB}$  greater than 8 c.p.s. However, for values of  $J_{AB}$  which are usually encountered (between 5 and 15 c.p.s.) the error involved in using eq. [2] only is not appreciable in view of the uncertainty in the measurement of  $i$ .

In any  $ABX$  system, when eq. [2] holds, the normal 12-line pattern degenerates to a simple 5-line spectrum in which the separation of the lines in the  $AB$  and  $X$  groups is equal to  $N$  i.e. the average of the two coupling constants  $J_{AX}$  and  $J_{BX}$ . The converse of this statement is equally important. This states that if an  $ABX$  system gives rise to a simple 5-line spectrum then the only constants that can be derived from the analysis of such a spectrum are the average values of  $J_{AX}$  and  $J_{BX}$ . It has been assumed previously (5) that if such a spectrum was obtained from an  $ABX$  system, then  $J_{AX} = J_{BX}$  and  $\delta = 0$ . We see, however, that this is only one set of values which interprets the spectrum and in general only  $J_{AX}/2$  and  $J_{BX}$  can be evaluated from the spacings.

The conditions for obtaining a 5-line spectrum in the 3-spin system  $ABX$  can be derived in an alternative manner. Consider the  $ABX$  system when  $L$  and  $\delta$  are small compared to  $J_{AB}$ . In this case, the parameters  $D_{\pm}$  in eq. [1a] can be written by neglecting higher powers of  $(\eta H_0 \delta \pm L)/J_{AB}$ . This gives

$$D_{\pm} = \frac{1}{2}J_{AB} + \frac{1}{4}(\eta H_0 \delta \pm L)^2 / J_{AB}$$

and

$$\sin 2\phi_{\pm} = 1 - \frac{1}{2} \left( \frac{\eta H_0 \delta \pm L}{J_{AB}} \right)^2$$

The energies and intensities in Table I can now be given directly in terms of  $\eta H_0 \delta$ ,  $L$ , and  $J_{AB}$  (Table II). The conditions necessary for the  $ABX$  system to give the 5-line

TABLE II  
Energies and intensities for  $ABX$  when  $L$  and  $\delta$  are small compared to  $J_{AB}$

Transition	Origin	Energy	Relative intensity
1	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-J_{AB}-(N/2)-\frac{1}{4}(\eta H_0\delta-L)^2/J_{AB}$	$\frac{1}{2}\left(\frac{\eta H_0\delta-L}{J_{AB}}\right)^2$
2	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-J_{AB}+(N/2)-\frac{1}{4}(\eta H_0\delta+L)^2/J_{AB}$	$\frac{1}{2}\left(\frac{\eta H_0\delta+L}{J_{AB}}\right)^2$
3	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-(N/2)-\frac{1}{4}(\eta H_0\delta-L)^2/J_{AB}$	2
4	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+(N/2)-\frac{1}{4}(\eta H_0\delta+L)^2/J_{AB}$	2
5	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)-(N/2)+\frac{1}{4}(\eta H_0\delta-L)^2/J_{AB}$	2
6	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+(N/2)+\frac{1}{4}(\eta H_0\delta+L)^2/J_{AB}$	2
7	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+J_{AB}-(N/2)+\frac{1}{4}(\eta H_0\delta-L)^2/J_{AB}$	$\frac{1}{2}\left(\frac{\eta H_0\delta-L}{J_{AB}}\right)^2$
8	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)+J_{AB}+(N/2)+\frac{1}{4}(\eta H_0\delta+L)^2/J_{AB}$	$\frac{1}{2}\left(\frac{\eta H_0\delta+L}{J_{AB}}\right)^2$
9	X	$\eta H_0(1-\sigma_X)-N$	1
10	X	$\eta H_0(1-\sigma_X)+\eta H_0\delta \cdot L/J_{AB}$	1
11	X	$\eta H_0(1-\sigma_X)-\eta H_0\delta \cdot L/J_{AB}$	1
12	X	$\eta H_0(1-\sigma_X)+N$	1

spectrum (eqs. [2] and [3]) are given by inspection of Table II. This table is of further use in the analysis of spectra in which transitions 4 and 6 may be resolved and some of the weaker lines can be observed (e.g. Fig. 1(b)), but in which  $L$  and  $\delta$  are still small compared to  $J_{AB}$ .

The results obtained in this analysis may be conveniently expressed in terms of a correlation diagram. Figure 1 shows (a) a typical 12-line  $ABX$  pattern, (b) the 11-line spectrum obtained when  $\delta$  or  $L = 0$ , and (c) the unresolved 5-line spectrum obtained when  $\delta$  and  $L$  are small compared to  $J_{AB}$ .

The different types of  $ABX$  spectrum mentioned above can sometimes be obtained for the same compound, merely by altering the relative chemical shift  $\delta$  by dissolving the compound in various solvents. Figure 2 shows the observed and calculated spectra for the  $ABX$  system of the ring protons of 2-furfural in three different environments, i.e. for three different values of  $\delta$ . Analysis of the spectrum 2c gives the following values for the coupling constants:  $J_{AB} = 3.16$  c.p.s.,  $J_{AX} = 1.89$  c.p.s., and  $J_{BX} = 0.91$  c.p.s. where A, B, and X represent protons 4, 3, and 5 respectively. In 2(a)  $\delta \rightarrow 0$  thus the spectrum is the simple 5-line spectrum since eq. [2] is valid. In 2(b)  $\delta = 1.83$  c.p.s. ( $\sigma_B > \sigma_A$ ). This value is such that eq. [1] no longer holds, i.e. the spectrum is not a simple one, but  $L$  and  $\delta$  are still small compared to  $J_{AB}$  thus the analysis of Table II can still be used and is in fact the most convenient method of analyzing the spectrum. In 2(c)  $\delta = 4.13$  c.p.s. and thus the spectrum is the full 12-line pattern. The dotted lines are drawn between corresponding transitions. It can be seen that all the B transitions (1.2.3.4) move together as do all the A lines (5.6.7.8). The actual values of the ring coupling constants used in the calculations were obtained from the analysis of the spectrum of Fig. 2(c).

The spectrum of the ring protons of liquid furfural at 40 Mc/sec has the simple 5-line pattern (5) and was interpreted previously (5) on the basis of  $L$  and  $\delta = 0$ . The value of  $\delta$  for liquid furfural at 60 Mc/sec = 1.83 c.p.s. (Fig. 2(b)). Thus the value of  $\delta$  at

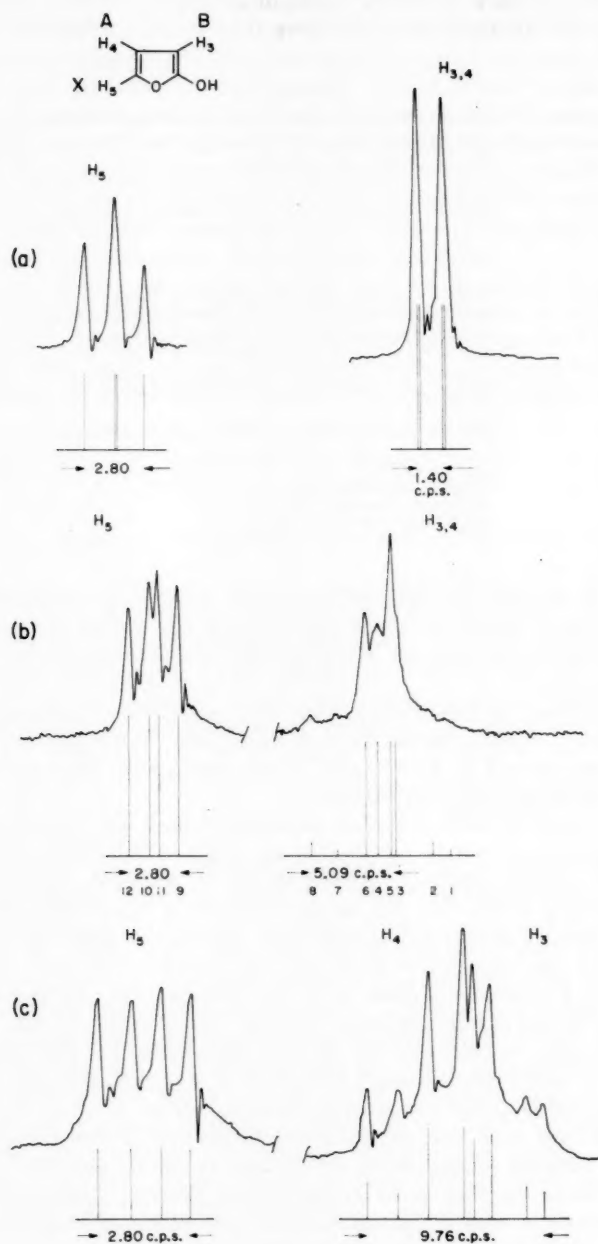


FIG. 2. Observed and calculated spectra of the ring protons of 2-furfulol at 60 Mc/sec: (a) in a 25% solution in benzene, (b) in the pure liquid, (c) in a 50% solution in dioxane.



40 Mc/sec = 1.21 c.p.s. Using this value and the values given above for the coupling constants, the left-hand side of eq. [2] becomes 0.40 c.p.s. Since this was about the limit of resolution of the instrument when the spectrum was obtained, it is understandable that the simple spectrum was observed. A further example of an  $ABX$  system giving the 5-line spectrum is the ring spectrum of 2,6-dichloro-3-fluorobenzotrifluoride (6) in which the spacing in the triplet and doublet is 6.2 c.p.s. (6). From the above consideration  $J_{\text{H}^{\text{Fortho}}} + J_{\text{H}^{\text{Fmeta}}} = 12.4$  c.p.s. Since the 5-line spectrum was obtained, eq. [2] gives

$$\frac{(J_{\text{H}^{\text{Fortho}}} - J_{\text{H}^{\text{Fmeta}}})^2}{2J_{AB}} < 0.3.$$

Assuming the spectrometer used was comparable to the Varian high-resolution instrument, and since  $J_{AB}$  is the spin coupling between adjacent protons in a benzene ring (ca. 8 c.p.s.),  $J_{\text{H}^{\text{Fortho}}} - J_{\text{H}^{\text{Fmeta}}} \leq 2.2$ , so that  $J_{\text{H}^{\text{Fortho}}} < 7.3$  and  $J_{\text{H}^{\text{Fmeta}}} > 5.1$  is the maximum information obtainable about the coupling constants from this spectrum. This example demonstrates that a 5-line spectrum can be obtained from a system in which the values of  $J_{AX}$  and  $J_{BX}$  are comparable to the value of  $J_{AB}$ .

Richards and Schaeffer also found very similar behavior in the spectra of some tri-substituted benzenes (7). In this case,  $ABC$ -type systems in which  $\delta_B \approx \delta_C$  were found to give spectra which approximate to the  $AB_2$  type, i.e. the spectrum has 5 lines characteristic of the  $AB_2$  pattern, not the many transitions obtained in the general  $ABC$  case. This is analogous behavior to the case considered above, which is essentially an  $ABX$  system giving an  $A_2X$  spectrum. Richards and Schaeffer used, in the analyses of these  $ABB'$  systems, pseudosymmetric wave functions i.e. the wave functions for the  $AB_2$  case were used and then two values of  $J_{AB}$  and  $J_{AB}'$  were introduced. This is an approximation and not a strictly rigorous treatment as some matrix elements were neglected. However, it is difficult to give a rigorous analysis in this case as the general  $ABC$  calculation does not give explicit values of the energies and intensities. The consequence of using pseudosymmetric wave functions in the  $ABX$  case is that only an 8-line spectrum (if the combination line is neglected) is obtained, 4  $X$  lines and 4  $AB$  lines. The weak transitions seen in the spectrum of Fig. 2(b), however, are to this approximation of zero intensity.

An equation analogous to eq. [2] can be written for these  $ABC$  systems, i.e. when

$$[4] \quad \frac{\{\delta_{BC} + \frac{1}{2}(J_{AB} - J_{AC})\}^2}{2J_{BC}} < \Delta\nu_{\frac{1}{2}}$$

the  $ABC$  system may be expected to give a spectrum of the  $AB_2$  type in which only the average of the coupling constants  $J_{AB}$  and  $J_{AC}$ , and the chemical shifts  $\sigma_B$  and  $\sigma_C$ , will be given explicitly. However, this equation has not been verified theoretically, though the experimental results of Richards and Schaeffer are not inconsistent with this statement.

#### The $A_2X_2$ Spectrum

The complete analysis for this system has already been given (2, 8) and is in a convenient form for the analysis of all possible types of spectra. Thus there is little value in formulating the complete energy level table under the conditions for which simple

spectra are obtained. However, the simple  $A_2X_2$  spectrum of two triplet groups which is obtained under certain conditions has been widely misinterpreted and thus the conditions for the formation of this simple spectrum will be considered in detail.

The nomenclature of reference 2 will be used.

The  $A_2X_2$  spectrum consists of two triplet groups when the separation between lines 10 and 11, and 6 and 7 is less than  $\Delta\nu_1$  and the intensities of lines 5, 8, 9, and 12 are less than  $i$ . These conditions are covered by the equations

$$[5] \quad (L^2/2M) < \Delta\delta_1$$

and

$$[6] \quad (L^2/4M^2) < i$$

where

$$L = J - J',$$

$$M = J_A - J_X.$$

In this case the separation between the lines in each triplet group will be equal to  $N/2$  i.e.  $\frac{1}{2}(J+J')$ .

As in the  $ABX$  case, eqs. [5] and [6] overlap, and again only eq. [5] will be considered.

As an example of the use of eq. [5], consider the spectrum of furan. This consists of two simple triplet groups and it has been widely interpreted (9, 10, 5, 6) as meaning that  $J_{23}(J)$  and  $J_{24}(J')$  are both equal to the line separation in the triplet groups, namely 1.3 c.p.s. (see Fig. 3 for the numbering of the protons). This is a possible interpretation

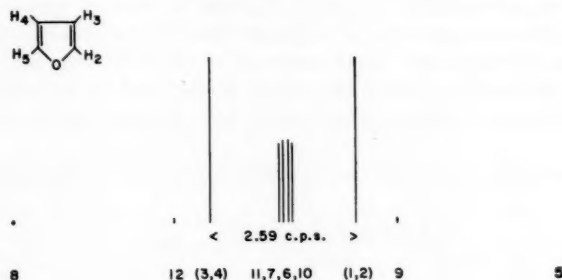


FIG. 3. The calculated spectrum of one of the triplet groups in furan.

of this spectrum. However, a more plausible interpretation can be obtained by considering the variation of coupling constants in the furan ring with substitution. It has been shown (11) that for a number of substituted furans the coupling constants are relatively insensitive to substitution and have the mean values  $J_{23}(J) = 1.80$  c.p.s.,  $J_{24}(J') = 0.80$  c.p.s.,  $J_{26}(J_X) = 1.55$  c.p.s., and  $J_{34}(J_A) = 3.53$  c.p.s. Using these values, eq. [5] holds and thus these coupling constants should explain the observed spectrum. In Fig. 3 the spectrum of furan, calculated with the above values of the coupling constants, is shown.

It is immediately apparent why the spectrum is observed as a simple triplet. The transitions labelled 5, 9, 8, and 12 are too weak to be observed and the spacings in the 11, 7, 6, 10 group are too small to be resolved. Strong support for this interpretation is the fact that the value of  $J+J'$  obtained experimentally from the furan spectrum (2.6 c.p.s.) agrees exactly with the value obtained independently from the spectra of the substituted furans.

Similar types of simple spectra, which give, however, more information about the coupling constants involved, are the proton resonance spectra of the compounds  $\text{CF}_2\text{X}-\text{CH}_2\text{X}$  where X is chlorine or bromine (12). These spectra have again essentially the triplet pattern but in these cases the center line is a doublet with a very small spacing. In these compounds  $J_{\text{FF}}$  is so much larger than  $J_{\text{HH}}$  that  $J_{\text{HH}}$  can be neglected and in this case the splitting of the central peak is equal to  $L^2/2J_{\text{FF}}$ . Once again, only the average value of  $J+J'$  can be found explicitly from the observed spectrum, but if  $J_{\text{FF}}$  can be estimated e.g. by analogy with similar compounds,  $L$  can be calculated and thus both  $J$  and  $J'$  can be found. In the bromo compound the splitting of the central peak is well resolved (0.6 c.p.s.) but in the chloro compound the splitting (0.25 c.p.s.) can only be estimated by an analysis of the beats. Note that in this case eq. [5] holds (i.e. with a resolution of 0.3 c.p.s. only the main triplet structure would be observed) even though  $L$  has the quite large value of 10 c.p.s.\* Using the formula given above gives the same results as Shoolery and Crawford for the chloro and iodo compounds, thus proving the validity of the approximation involved in neglecting  $J_{\text{HH}}$ , but the value for  $L$  obtained for the bromo compound is 14.5 c.p.s. Thus  $J_{\text{T}} = 20$ , and  $J_{\text{C}} = 6$  c.p.s. respectively. The slight difference from the reported values is due to an arithmetical error (12). Here we have preferred  $J_{\text{T}} > J_{\text{C}}$  in keeping with our unpublished results on the relative sizes of  $J_{\text{T}}$  and  $J_{\text{C}}$  in 1,1,2,2-tetrachloro-1-fluoroethane.†

### The ABXY Spectrum

The ABX analysis considered earlier shows that a simple spectrum is obtained when  $J_{\text{AB}}$  is large compared to  $\delta_{\text{AB}}$  and  $J_{\text{AX}}-J_{\text{BX}}$ . The same general statement is true for the  $\text{A}_2\text{X}_2$  system remembering that in this case due to the symmetry of the system, the actual functions involved in the analysis are sums and differences of the coupling constants. By analogy, an ABXY system will be expected to give a simple spectrum when  $J_{\text{AB}}$  and  $J_{\text{XY}}$  are large compared to  $\delta_{\text{AB}}$ ,  $\delta_{\text{XY}}$  and terms like  $J_{\text{AX}}-J_{\text{BX}}$ .

The quantitative expression of this statement will now be derived. The transition energies and intensities for the ABXY system cannot be derived explicitly in the general case as this involves solving a  $4 \times 4$  determinant. However, in the case considered here, this  $4 \times 4$  determinant can be solved explicitly and thus the energies and intensities can be written down completely.

This calculation follows the procedure laid down in reference 1. The basic functions, diagonal elements, and off-diagonal elements needed are given in Table III. Some off-diagonal elements, e.g.  $\mathfrak{S}_{24}$  are not given as they are not involved in the calculation. These basic functions do not mix when (a) there is a difference in the total spin quantum number (this separation is shown by the full lines) and (b) there is an energy difference of the form  $\delta_{\text{A}}-\delta_{\text{X}}$  (this is shown by the dotted lines in Table III).

\* $L$  is defined in reference 12 as  $\frac{1}{2}(J+J')$  thus it has one-half the value of  $L$  used here.

†Given at the Symposium on Molecular Spectra, Columbus, Ohio, June 1959.

TABLE III  
Basic functions and matrix elements for  $ABXY$

$ABXY$	$F$	Diagonal	Matrix elements*					
			$\frac{1}{2}J_{AB}$	$\frac{1}{2}J_{AX}$	$\frac{1}{2}J_{AY}$	$\frac{1}{2}J_{BX}$	$\frac{1}{2}J_{BY}$	$\frac{1}{2}J_{XY}$
1	$\alpha\alpha\alpha\alpha$	2	$(\nu_0/2)(H_A+H_B+H_X+H_Y)$	+	+	+	+	+
2	$\alpha\alpha\alpha\beta$	1	$(\nu_0/2)(H_A+H_B+H_X+H_Y)$	+	+	-	+	-
3	$\alpha\alpha\beta\alpha$	1	$(\nu_0/2)(H_A+H_B-H_X+H_Y)$	+	-	+	-	-
4	$\alpha\beta\alpha\alpha$	1	$(\nu_0/2)(H_A-H_B+H_X+H_Y)$	-	+	+	-	+
5	$\beta\alpha\alpha\alpha$	1	$(\nu_0/2)(-H_A+H_B+H_X+H_Y)$	-	-	-	+	+
6	$\alpha\alpha\beta\beta$	0	$(\nu_0/2)(H_A+H_B-H_X-H_Y)$	+	-	-	-	+
7	$\alpha\beta\alpha\beta$	0	$(\nu_0/2)(H_A-H_B+H_X-H_Y)$	-	+	-	-	-
8	$\alpha\beta\beta\alpha$	0	$(\nu_0/2)(H_A-H_B-H_X+H_Y)$	-	-	+	+	-
9	$\beta\alpha\alpha\beta$	0	$(\nu_0/2)(-H_A+H_B+H_X-H_Y)$	-	-	+	+	-
10	$\beta\alpha\beta\alpha$	0	$(\nu_0/2)(-H_A+H_B-H_X+H_Y)$	-	+	-	-	-
11	$\beta\beta\alpha\alpha$	0	$(\nu_0/2)(-H_A-H_B+H_X+H_Y)$	+	-	-	-	+
12	$\alpha\beta\beta\beta$	-1	$(\nu_0/2)(H_A-H_B-H_X-H_Y)$	-	-	-	+	+
13	$\beta\alpha\beta\beta$	-1	$(\nu_0/2)(-H_A+H_B-H_X-H_Y)$	-	+	+	-	+
14	$\beta\beta\alpha\beta$	-1	$(\nu_0/2)(-H_A-H_B+H_X-H_Y)$	+	-	+	-	-
15	$\beta\beta\beta\alpha$	-1	$(\nu_0/2)(-H_A-H_B-H_X+H_Y)$	+	+	-	+	-
16	$\beta\beta\beta\beta$	-2	$(\nu_0/2)(-H_A-H_B-H_X-H_Y)$	+	+	+	+	+

Off-diagonal matrix elements

$\mathfrak{S}_{2,3} = \frac{1}{2}J_{XY},$	$\mathfrak{S}_{4,5} = \frac{1}{2}J_{AB}$	$\mathfrak{S}_{7,10} = 0$
$\mathfrak{S}_{7,8} = \frac{1}{2}J_{XY},$	$\mathfrak{S}_{7,9} = \frac{1}{2}J_{AB},$	
$\mathfrak{S}_{8,9} = 0,$	$\mathfrak{S}_{8,10} = \frac{1}{2}J_{AB}$	
$\mathfrak{S}_{9,10} = \frac{1}{2}J_{XY}$		
$\mathfrak{S}_{12,13} = \frac{1}{2}J_{AB},$	$\mathfrak{S}_{14,15} = \frac{1}{2}J_{XY}$	

\*The + and - signs represent +1 and -1 respectively.

Thus to determine the energies and wave functions in this case four  $2 \times 2$  determinants and one  $4 \times 4$  determinant have to be solved.

The former can be solved explicitly. It is convenient to define the following constants.

$$\begin{aligned}
 L &= \frac{1}{2}(J_{AX} - J_{AY}) & R &= \frac{1}{2}(J_{BX} + J_{BY}) \\
 T &= \frac{1}{2}(J_{BX} - J_{BY}) & M &= \frac{1}{2}(J_{AB} - J_{XY}) \\
 N &= \frac{1}{2}(J_{AX} + J_{AY}) & K &= \frac{1}{2}(J_{AB} + J_{XY}) \\
 \delta_{AB} &= \nu_0(H_A - H_B) & \delta_{XY} &= \nu_0(H_X - H_Y)
 \end{aligned}$$

and

$$\begin{aligned}
 C_{\pm} \cos 2\phi_{\pm} &= \frac{1}{2}\delta_{XY} \pm \frac{1}{2}(L + T) \\
 C_{\pm} \sin 2\phi_{\pm} &= \frac{1}{2}J_{XY} \\
 D_{\pm} \cos 2\phi_{\pm} &= \frac{1}{2}\delta_{AB} \pm \frac{1}{2}(N - R) \\
 D_{\pm} \sin 2\phi_{\pm} &= \frac{1}{2}J_{AB}
 \end{aligned}$$

The energy levels and wave functions for all the states except 7, 8, 9, and 10 can now be given in terms of these quantities (Table IV). These have been derived for the

TABLE IV  
Explicit energies and wave functions for  $ABXY$

Energy		Wave function*
1	$(\nu_0/2)(H_A+H_B+H_X+H_Y)+\frac{1}{2}(K+N+R)$	(1)
2'	$(\nu_0/2)(H_A+H_B)+\frac{1}{2}M+C+$	$\cos \theta_+(2)+\sin \theta_+(3)$
3'	$(\nu_0/2)(H_A+H_B)+\frac{1}{2}M-C+$	$-\sin \theta_+(2)+\cos \theta_+(3)$
4'	$(\nu_0/2)(H_X+H_Y)-\frac{1}{2}M+D+$	$\cos \phi_+(4)+\sin \phi_+(5)$
5'	$(\nu_0/2)(H_X+H_Y)-\frac{1}{2}M-D+$	$-\sin \phi_+(4)+\cos \phi_+(5)$
6'	$(\nu_0/2)(H_A+H_B-H_X-H_Y)+\frac{1}{2}(K-N-R)$	(6)
7'	$K/2$	$(\frac{1}{2}+p)(7)+(\frac{1}{2}+q)(8)+(\frac{1}{2}-q)(9)+(\frac{1}{2}-p)(10)$
8'	$-\frac{1}{2}K+M$	$(-\frac{1}{2}-q)(7)+(\frac{1}{2}+p)(8)+(-\frac{1}{2}+p)(9)+(\frac{1}{2}-q)(10)$
9'	$-\frac{1}{2}K-M$	$(-\frac{1}{2}+q)(7)+(-\frac{1}{2}+p)(8)+(\frac{1}{2}+p)(9)+(\frac{1}{2}+q)(10)$
10'	$-3/2K$	$(\frac{1}{2}-p)(7)+(-\frac{1}{2}+q)(8)+(-\frac{1}{2}-q)(9)+(\frac{1}{2}+p)(10)$
11	$(\nu_0/2)(-H_A-H_B+H_X+H_Y)+\frac{1}{2}(K-N-R)$	(11)
12'	$(\nu_0/2)(-H_X-H_Y)-\frac{1}{2}M+D-$	$\cos \phi_-(12)+\sin \phi_-(13)$
13'	$(\nu_0/2)(-H_X-H_Y)-\frac{1}{2}M-D-$	$-\sin \phi_-(12)+\cos \phi_-(13)$
14'	$(\nu_0/2)(-H_A-H_B)+\frac{1}{2}M+C-$	$\cos \theta_-(14)+\sin \theta_-(15)$
15'	$(\nu_0/2)(-H_A-H_B)+\frac{1}{2}M-C-$	$-\sin \theta_-(14)+\cos \theta_-(15)$
16	$(\nu_0/2)(-H_A-H_B-H_X-H_Y)+\frac{1}{2}(K+N+R)$	(16)
$p = \frac{\Delta}{8} \left( \frac{1}{J_{AB}} + \frac{1}{J_{XY}} \right)$		$q = \frac{\Delta}{8} \left( \frac{1}{J_{AB}} - \frac{1}{J_{XY}} \right)$

\*The numbers in parentheses refer to the spin functions given in Table III.

general  $ABXY$  system. However, in order to solve the  $4 \times 4$  secular determinant (eq. [7]), the case for which  $L$ ,  $T$ ,  $\delta_{AB}$ , and  $\delta_{XY}$  are small compared to  $J_{XY}$  and  $J_{AB}$ , must be considered.

$$[7] \begin{vmatrix} \frac{1}{2}(\delta_{AB}+\delta_{XY}-K+L-T)-E & \frac{1}{2}J_{XY} & \frac{1}{2}J_{AB} & 0 \\ \frac{1}{2}J_{XY} & \frac{1}{2}(\delta_{AB}-\delta_{XY}-K-L+T)-E & 0 & \frac{1}{2}J_{AB} \\ \frac{1}{2}J_{AB} & 0 & \frac{1}{2}(-\delta_{AB}+\delta_{XY}-K-L+T)-E & \frac{1}{2}J_{XY} \\ 0 & \frac{1}{2}J_{AB} & \frac{1}{2}J_{XY} & \frac{1}{2}(-\delta_{AB}-\delta_{XY}-K+L-T)-E \end{vmatrix} = 0$$

The difference of two small quantities, i.e.  $\delta_{AB}-\delta_{XY}$  and  $L-T$  in eq. [7], will be neglected. Thus, defining

$$F = -K-2E \quad \text{and} \quad \Delta = \delta_{AB}+\delta_{XY}$$

eq. [7] becomes

$$[8] \begin{vmatrix} \Delta+F & J_{XY} & J_{AB} & 0 \\ J_{XY} & F & 0 & J_{AB} \\ J_{AB} & 0 & F & J_{XY} \\ 0 & J_{AB} & J_{XY} & -\Delta+F \end{vmatrix} = 0$$

Expanding this determinant and reuniting in terms of  $M$  and  $K$  gives

$$F^4 - 4F^2[K^2 + M^2 + (\Delta^2/4)] + 16M^2K^2 = 0.$$

Neglecting  $(\Delta/2)^2$  with respect to  $K^2 + M^2$  gives the roots

$$F = \pm 2K; \quad \pm 2M$$

and thus the energies of the states 7', 8', 9', and 10'.



The wave functions for these states are given by introducing these energy values successively in eq. [8] and solving the four simultaneous equations obtained using the normalizing condition for the coefficients of the basic functions, neglecting  $\Delta^2$  when it occurs. The complete wave functions and energies are given in Table IV. As we have included now (for states 7', 8', 9', and 10') the condition of  $L$ ,  $T$ ,  $\delta_{AB}$ , and  $\delta_{XY}$  being small compared to  $J_{AB}$  and  $J_{XY}$ , we will consider how the energies and intensities of the remaining states change when this condition holds before giving the transition energies and intensities. When this condition holds,

$$C_{\pm} = \frac{1}{2}J_{XY}\{1 + \frac{1}{2}(\alpha_{\pm}/J_{XY})^2\},$$

$$D_{\pm} = \frac{1}{2}J_{AB}\{1 + \frac{1}{2}(\beta_{\pm}/J_{AB})^2\},$$

and

$$(\cos \theta_{\pm} - \sin \theta_{\pm})^2 = \frac{1}{2}(\alpha_{\pm}/J_{XY})^2,$$

$$(\cos \phi_{\pm} - \sin \phi_{\pm})^2 = \frac{1}{2}(\beta_{\pm}/J_{AB})^2,$$

$$(\cos \theta_{\pm} + \sin \theta_{\pm})^2 = (\cos \phi_{\pm} + \sin \phi_{\pm})^2 = 2,$$

where

$$\alpha_{\pm} = \delta_{XY} \pm (L+T),$$

$$\beta_{\pm} = \delta_{AB} \pm (N-R).$$

The transition energies and intensities can be derived simply from Table IV. Including in these expressions the above equations gives the transition energies and relative intensities explicitly for the  $ABXY$  system in the case considered. These are shown in Table V.

Table V is in the same form as Table II for the  $ABX$  case and the type of spectrum obtained when Table V is valid (the  $AB$  part is shown in Fig. 4(b)) is very similar in form to the  $AB$  part of the spectrum of Fig. 2(b). The spectrum of Fig. 4(b) approximates to that of a simple triplet group (Fig. 4(c)) and the conditions under which this simple spectrum is obtained can be derived in exactly the same manner as in the  $ABX$  case. The conditions under which an  $ABXY$  system will give a simple spectrum of two triplet groups are

$$[9] \quad \{\delta_{XY} + (L+T)\}^2 / 2J_{XY} < \Delta\nu_1,$$

$$[10] \quad \{\delta_{AB} + (N-R)\}^2 / 2J_{AB} < \Delta\nu_1,$$

and

$$\frac{1}{2}\{(\delta_{XY} + L+T)/J_{XY}\}^2 < i,$$

$$[11] \quad \frac{1}{2}\{(\delta_{AB} + N-R)/J_{AB}\}^2 < i,$$

$$\frac{1}{2}\{(\delta_{AB} + \delta_{XY})/2J_{AB}\}^2 < i,$$

$$\frac{1}{2}\{(\delta_{AB} + \delta_{XY})/2J_{XY}\}^2 < i,$$

and when these conditions hold, the spacing in the triplet groups is equal to  $\frac{1}{2}(N+R)$ .

These results may also be conveniently expressed in the form of a correlation diagram (Fig. 4). This gives the  $AB$  part of an  $ABXY$  spectrum (the  $XY$  half will be very similar), and in this case, as the general  $ABXY$  spectrum cannot be given explicitly, Fig. 4(a) gives the  $AB$  spectrum in the first-order approximation when  $\delta_{AB}$  and  $\delta_{XY}$  are large compared to the coupling constants. In Fig. 4(b), the spectrum is given when Table V

TABLE V  
Energies and intensities for  $ABXY$

		Energy	Relative intensity
<b>A Transitions</b>			
(a)	$5' \rightarrow 1$	$(\nu_0/2)(H_A + H_B) + J_{AB} + \frac{1}{2}(N+R) + \frac{1}{4}\beta_+^2/J_{AB}$	$\frac{1}{2}(\beta_+/J_{AB})^2$
(b)	$9' \rightarrow 2'$	$" + J_{AB} + \frac{1}{4}\alpha_+^2/J_{XY}$	$\frac{1}{2}(\Delta/2J_{AB})^2$
(c)	$10' \rightarrow 3'$	$" + J_{AB} - \frac{1}{4}\alpha_+^2/J_{XY}$	$\frac{1}{2}(\Delta/2J_{AB})^2$
(d)	$11 \rightarrow 4'$	$" + \frac{1}{2}(N+R) + \frac{1}{4}\beta_+^2/J_{AB}$	2
(e)	$13' \rightarrow 6$	$" + J_{AB} - \frac{1}{2}(N+R) + \frac{1}{4}\beta_-^2/J_{AB}$	$\frac{1}{2}(\beta_-/J_{AB})^2$
(f)	$14' \rightarrow 7'$	$" - \frac{1}{4}\alpha_-^2/J_{XY}$	$2 + \alpha_-/2J_{XY}^2(\Delta - \alpha_-)$
(g)	$15' \rightarrow 8'$	$" + \frac{1}{4}\alpha_-^2/J_{XY}$	$2 + \alpha_-/2J_{XY}^2(\Delta - \alpha_-)$
(h)	$16 \rightarrow 12'$	$" - \frac{1}{2}(N+R) + \frac{1}{4}\beta_-^2/J_{AB}$	2
<b>B Transitions</b>			
(a)	$4' \rightarrow 1$	$(\nu_0/2)(H_A + H_B) + \frac{1}{2}(N+R) - \frac{1}{4}\beta_+^2/J_{AB}$	2
(b)	$7' \rightarrow 2'$	$" + \frac{1}{4}\alpha_+^2/J_{XY}$	$2 + \alpha_+/2J_{XY}^2(\Delta - \alpha_+)$
(c)	$8' \rightarrow 3'$	$" - \frac{1}{4}\alpha_+^2/J_{XY}$	$2 + \alpha_+/2J_{XY}^2(\Delta - \alpha_+)$
(d)	$11 \rightarrow 5'$	$" - J_{AB} + \frac{1}{2}(N+R) - \frac{1}{4}\beta_+^2/J_{AB}$	$\frac{1}{2}(\beta_+/J_{AB})^2$
(e)	$12' \rightarrow 6$	$" - \frac{1}{2}(N+R) - \frac{1}{4}\beta_-^2/J_{AB}$	2
(f)	$14' \rightarrow 9'$	$" - J_{AB} - \frac{1}{4}\alpha_-^2/J_{XY}$	$\frac{1}{2}(\Delta/2J_{AB})^2$
(g)	$15' \rightarrow 10'$	$" - J_{AB} + \frac{1}{4}\alpha_-^2/J_{XY}$	$\frac{1}{2}(\Delta/2J_{AB})^2$
(h)	$16 \rightarrow 13'$	$" - J_{AB} - \frac{1}{2}(N+R) - \frac{1}{4}\beta_-^2/J_{AB}$	$\frac{1}{2}(\beta_-/J_{AB})^2$
<b>X Transitions</b>			
(a)	$3' \rightarrow 1$	$(\nu_0/2)(H_X + H_Y) + J_{XY} + \frac{1}{2}(N+R) + \frac{1}{4}\alpha_+^2/J_{XY}$	$\frac{1}{2}(\alpha_+/J_{XY})^2$
(b)	$6 \rightarrow 2'$	$" + \frac{1}{2}(N+R) + \frac{1}{4}\alpha_+^2/J_{XY}$	2
(c)	$8' \rightarrow 4'$	$" + J_{XY} + \frac{1}{4}\beta_+^2/J_{AB}$	$\frac{1}{2}(\Delta/2J_{XY})^2$
(d)	$10' \rightarrow 5'$	$" + J_{XY} - \frac{1}{4}\beta_+^2/J_{AB}$	$\frac{1}{2}(\Delta/2J_{XY})^2$
(e)	$12' \rightarrow 7'$	$" - \frac{1}{2}\beta_-^2/J_{AB}$	$2 + \beta_-/2J_{AB}^2(\Delta - \beta_-)$
(f)	$13' \rightarrow 9'$	$" + \frac{1}{2}\beta_-^2/J_{AB}$	$2 + \beta_-/2J_{AB}^2(\Delta - \beta_-)$
(g)	$15' \rightarrow 11$	$" + J_{XY} - \frac{1}{2}(N+R) + \frac{1}{4}\alpha_-^2/J_{XY}$	$\frac{1}{2}(\alpha_-/J_{XY})^2$
(h)	$16 \rightarrow 14'$	$" - \frac{1}{2}(N+R) + \frac{1}{4}\alpha_-^2/J_{XY}$	2
<b>Y Transitions</b>			
(a)	$2' \rightarrow 1$	$(\nu_0/2)(H_X + H_Y) + \frac{1}{2}(N+R) - \frac{1}{4}\alpha_+^2/J_{XY}$	2
(b)	$6 \rightarrow 3'$	$" - J_{XY} + \frac{1}{2}(N+R) - \frac{1}{4}\alpha_+^2/J_{XY}$	$\frac{1}{2}(\alpha_+/J_{XY})^2$
(c)	$7' \rightarrow 4'$	$" + \frac{1}{4}\beta_+^2/J_{AB}$	$2 + \beta_+/2J_{AB}^2(\Delta - \beta_+)$
(d)	$9' \rightarrow 5'$	$" - \frac{1}{4}\beta_+^2/J_{AB}$	$2 + \beta_+/2J_{AB}^2(\Delta - \beta_+)$
(e)	$12' \rightarrow 8'$	$" - J_{XY} - \frac{1}{4}\beta_-^2/J_{AB}$	$\frac{1}{2}(\Delta/2J_{XY})^2$
(f)	$13' \rightarrow 10'$	$" - J_{XY} + \frac{1}{4}\beta_-^2/J_{AB}$	$\frac{1}{2}(\Delta/2J_{XY})^2$
(g)	$14' \rightarrow 11$	$" - \frac{1}{2}(N+R) - \frac{1}{4}\alpha_-^2/J_{XY}$	2
(h)	$16 \rightarrow 15'$	$" - J_{XY} - \frac{1}{2}(N+R) - \frac{1}{4}\alpha_-^2/J_{XY}$	$\frac{1}{2}(\alpha_-/J_{XY})^2$

is valid, i.e.  $L$ ,  $T$ ,  $\delta_{AB}$ , and  $\delta_{XY}$  are small compared to  $J_{AB}$  and  $J_{XY}$ , but eqs. [9], [10], and [11] do not hold, and in Fig. 4(c) is shown the simple 3-line spectrum obtained when eqs. [9], [10], and [11] are valid. The actual values of the coupling constants  $J_{AB}$ ,  $J_{XY}$ ,  $J_{AX}$ ,  $J_{AY}$ ,  $J_{BX}$ , and  $J_{BY}$  used in Fig. 4 were 10, 12, 9.5, 8.5, 9.5, and 4.5 c.p.s., respectively, and the chemical shift values are  $\delta_{AB} = 48$  c.p.s. in Fig. 4(a) ( $\delta_{XY}$  is not involved in this case),  $\delta_{AB} = 3$  c.p.s., and  $\delta_{XY} = 4$  c.p.s. in Fig. 4(b), and  $\delta_{AB} = \delta_{XY} = 0$  c.p.s. in Fig. 4(c).

The calculations in this section have given the quantitative condition necessary in order that the  $ABXY$  system will give a simple spectrum, and it is seen that the assumption made in the beginning of this section, i.e. that the simple spectrum is obtained when  $J_{AB}$  and  $J_{XY}$  are large compared to terms like  $\delta_{AB}$ ,  $\delta_{XY}$ , and  $J_{AX} - J_{BX}$ , which was obtained merely by inspection of the results for the  $ABX$  and  $A_2X_2$  systems, is valid. In the next section, the results for the three systems considered are compared in order to obtain the general condition necessary for these simple spectra to be obtained.

#### The General Case

The conditions under which the  $ABX$ ,  $A_2X_2$ , and  $ABXY$  systems give these deceptively

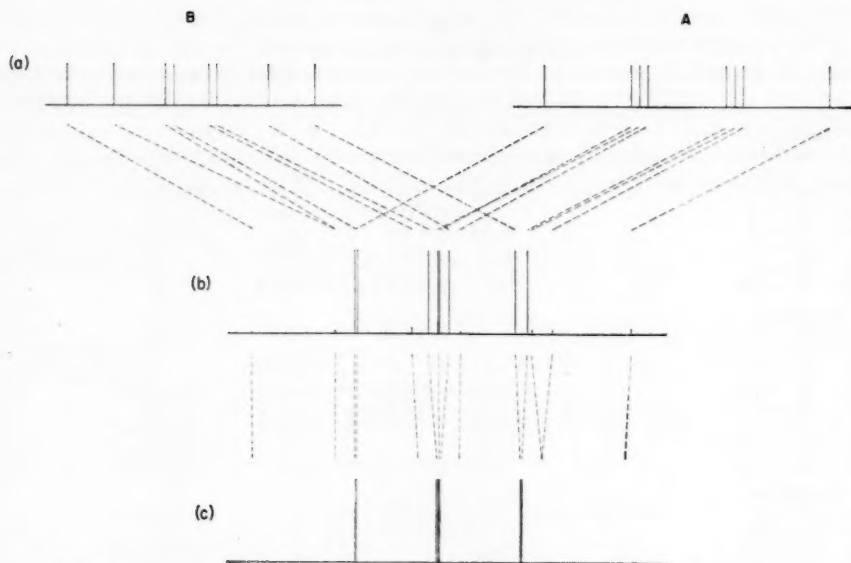


FIG. 4. Typical spectra of the  $AB$  part of the  $ABXY$  system when (a)  $\delta_{AB}$  and  $\delta_{XY}$  are large compared to  $J_{AB}$  and  $J_{XY}$ ; (b)  $J_{AB}$  and  $J_{XY}$  are large compared to  $\delta_{AB}$ ,  $\delta_{XY}$ ,  $L$ , and  $T$ ; (c) equations [7] and [8] are valid.

simple spectra (eqs. [2], [5], [9], and [10]), can be compared most easily by rewriting these equations in terms of the actual coupling constants involved. These equations become

$$[2a] \quad \{\delta_{AB} + \frac{1}{2}(J_{AX} - J_{BX})\}^2 / 2J_{AB} < \Delta\nu_1,$$

$$[5a] \quad (J - J')^2 / 2(J_A - J_X) < \Delta\nu_1,$$

$$[9a] \quad \{\delta_{XY} + \frac{1}{2}(J_{AX} - J_{AY} + J_{BX} - J_{BY})\}^2 / 2J_{XY} < \Delta\nu_1,$$

$$[10a] \quad \{\delta_{AB} + \frac{1}{2}(J_{AX} - J_{BX} + J_{AY} - J_{BY})\}^2 / 2J_{AB} < \Delta\nu_1.$$

It can be seen that eqs. [2a] and [10a] are equivalent, but the latter has extra terms involving the new nucleus  $Y$  which are of the same form as those involving  $X$  in eq. [2a]. This result shows that any general condition valid for the  $ABXY$  case will also be valid for the  $ABX$  case merely by removing the terms in  $Y$  and also it indicates that one explicit condition for the  $ABXYZ \dots$  system to give a simple spectrum will be

$$[12] \quad \{\delta_{AB} + \frac{1}{2}(J_{AX} - J_{BX} + J_{AY} - J_{BY} + J_{AZ} - J_{BZ} + \dots)\}^2 / J_{AB} < \Delta\nu_1.$$

The conditions necessary for the general system  $ABC \dots XYZ \dots$  to give a simple spectrum cannot, however, be derived explicitly, but from the form of the equations above, the nature of these conditions may be given in a qualitative fashion, as follows. The system  $ABC \dots XYZ \dots$  will be expected to give a simple spectrum when the terms of the type  $J_{AB}$ ,  $J_{XY}$  are large compared to the chemical shift differences  $\delta_{AB}$ ,  $\delta_{XY}$  plus terms of the form  $J_{AX} - J_{AY}$ , etc. and in this case the spectrum will be a simple first-order  $A_m X_n$  spectrum in which the separation of the lines in each group of the spectrum is given by the average of the coupling constants  $J_{AX}$ ,  $J_{AY}$ , etc.

This statement has to be modified when the system has some elements of symmetry. This can be seen in the above equations, since eq. [5a] for the  $A_2X_2$  system cannot be derived from either eqs. [9a] or [10a] for the  $ABXY$  system. This is due to the fact that the element of symmetry in the  $A_2X_2$  case causes all the matrix elements in the calculation to appear as sums or differences of the actual coupling constants involved. However, the form of eqs. [5a], [9a], and [10a] is very similar and thus the same type of statement will be true in the symmetric case, but sums and differences of the actual coupling constants may be involved. Some examples of this general statement will now be considered.

The system of the ring protons and the fluorine nucleus in *p*-fluorotoluene is an  $A_2B_2X$  system. (The protons meta to the fluorine will be termed the *A* protons.) This system has been analyzed in detail by Schaeffer (13) and the general spectrum has a total of 64 transitions. However, the spectrum of liquid *p*-fluorotoluene consists of a doublet ring proton spectrum (at 30 Mc/sec) and a complex fluorine spectrum which after removing the coupling with the methyl group is the quintet characteristic of a first-order  $A_4X$  spectrum. Schaeffer (13) has interpreted this on the basis of equal coupling constants  $J_{AX}$  and  $J_{BX}$ . However, this is not the only interpretation of this spectrum. The cross-ring proton-proton coupling constants in the benzene ring are small and thus this system can be treated approximately as an  $ABX$  system. With the normal values (6) of the coupling constants in the benzene ring of  $J_{AB} = 7.9$ ,  $J_{AX} = 7.0$ , and  $J_{BX} = 8.6$  c.p.s., respectively, we find eq. [2] to be valid for this system if  $\delta_{AB}$  is less than 1 c.p.s. The observed spectrum demonstrates that this must be the case and the separation of the lines in each group of the spectrum (7.4 c.p.s.) is in good agreement with the calculated value of  $\frac{1}{2}(J_{AX} + J_{BX})$ . Further results (14) in which the chemical shift difference between the *A* and *B* protons has been increased by dissolving the compound in various solvents giving rise to a more complex spectrum confirm this latter interpretation. The interpretation based on the equality of the ortho and meta coupling constants, whilst a possible explanation of the liquid spectrum, is not consistent with the analyses of the more complex spectra observed in solutions.

The spectrum of fluorobenzene is an example of an  $AB_2C_2X$  spectrum, and the usual values (6) of the ring coupling constants for this system are  $J_{AB} = J_{BC} = 7.9$ ,  $J_{AC} = 2.1$ ,  $J_{AX} = 2.2$ ,  $J_{BX} = 7.0$ ,  $J_{CX} = 8.6$  c.p.s., respectively. Thus  $J_{AB}$  and  $J_{BC}$  are larger than  $J_{AX} - J_{BX}$  and  $J_{BX} - J_{CX}$ , etc. and if  $\delta_{AB}$  and  $\delta_{BC}$  are sufficiently small the general statement above will hold. The proton spectrum of this compound will then be expected to be a doublet and the fluorine spectrum a sextet characteristic of an  $A_6X$  spectrum with the separation in each group equal to  $\frac{1}{3}(J_{AX} + 2J_{BX} + 2J_{CX})$ , i.e. 6.6 c.p.s. The observed proton spectrum at 40 Mc/sec and  $F^{19}$  spectrum at 30 Mc/sec (15, 16, 17) agrees with these expectations. Thus the values of  $\delta_{AB}$  etc. are so small that the general statement (eq. [12]) does hold and the observed value of the separation in each group of 6.5 c.p.s. agrees very well with the calculated value. This explanation of the spectrum has also been proposed by Roux (17), on similar arguments.

The spectrum of benzene- $d_1$  (Fig. 5) is also an example of an  $AB_2C_2X$  system and in this case  $\delta_{AB} = \delta_{BC}$ . Also  $J_{AB}$ ,  $J_{BC}$ , and  $J_{AC}$  will be larger than any of the proton-deuterium coupling constants  $J_{BX}$  etc. and therefore much larger than terms of the type  $J_{AX} - J_{BX}$ . Thus again eq. [12] is valid and the proton spectrum of this compound will be expected to be a triplet of spacing  $\frac{1}{3}(J_{AX} + 2J_{BX} + 2J_{CX})$ . The normal values (18) of  $J_{AX}$ ,  $J_{BX}$ , and  $J_{CX}$  are 0.1, 0.34, and 1.21 c.p.s., respectively, which give a triplet

spacing of 0.64 c.p.s.\* The observed proton spectrum of this compound is given in Fig. 5 and the triplet spacing of 0.55 c.p.s. agrees excellently with the predicted value.

The above result for benzene- $d_1$  may be extended to almost any monodeutero-substituted compound as in these compounds the proton-deuterium coupling constants will be much less than the proton-proton coupling constants. Thus in these compounds the general statement above will apply and therefore monodeuterium substitution in a molecule containing more than two hydrogen atoms will generally only give the average of all the proton-deuterium couplings which are present in the molecule.

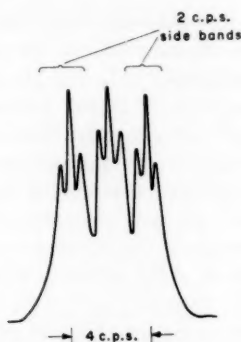


FIG. 5. The proton spectrum of liquid benzene- $d_1$  at 60 Mc/sec with a 2 c.p.s. side band.

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\*The proton-proton spin coupling constants have been divided by  $U_H I_D / U_D I_H$  to obtain the corresponding deuterium-proton spin coupling constants.  $U_H$  is the magnetic moment and  $I_H$  is the spin of the proton and  $U_D$  and  $I_D$  the corresponding quantities for the deutron.



# THE PREPARATION, PAPER CHROMATOGRAPHY, AND COLOR REACTIONS OF SEVERAL 5,6-DIHYDROXYINDOLES AND 5,6-DIACETOXYINDOLES<sup>1</sup>

R. A. HEACOCK, M. E. MAHON, AND B. D. SCOTT

## ABSTRACT

The paper chromatographic behavior of several 5,6-dihydroxyindoles has been studied. The colors given by nine dihydroxyindoles with 16 chromogenic reagents are reported. The  $R_f$  values of this group of compounds on Whatman No. 1 paper with 2% acetic acid in water or *n*-butanol/acetic acid/water (6:1:2) as running solvents have been determined. The 5,6-dihydroxyindoles can be chromatographed satisfactorily using Zaffaroni-type systems (i.e. formamide-treated paper and non-polar running solvents). Satisfactory  $R_f$  values can also be obtained for the 5,6-diacetoxyindoles on formamide-treated paper using a suitable non-polar mobile phase. The preparations of several new 5,6-dihydroxyindoles and 5,6-diacetoxyindoles are described and improved procedures for the syntheses of some known members of these groups are reported.

The importance of the 5,6-dihydroxyindoles as intermediates in the production of the dark pigments known as melanins, in plants and animals, has been recognized for some time (for references see reviews by Lerner (1), Mason (2), and Thomas (3)), but it is only in relatively recent years that many of these highly reactive compounds have been obtained in pure crystalline form (see (3) and (4) for references). Although there has been a considerable volume of work carried out on the chromatography of the indoles in the past decade, there have been relatively few studies reported of the paper chromatographic behavior of the 5,6-dihydroxyindoles and their derivatives. In a study of the urine melanogens observed in cases of malignant melanoma of the liver, Leonhardi reported the  $R_f$  values of some 5,6-dihydroxyindole derivatives (e.g. *O*-acetyl, *O*-methyl, *O*-sulphatoxy, etc.) in several different solvent systems. These compounds were employed as models for the urinary melanogens which were considered by Leonhardi to be 5,6-dihydroxyindole derivatives (5). During an investigation into the metabolism of  $\beta$ -(3,4-dihydroxyphenyl)-alanine in albino rats Pellerin and D'Iorio obtained a product with a  $R_f$  of 0.85 in a *n*-butanol/acetic acid/water system which they suggested was possibly 5,6-dihydroxyindole (6).

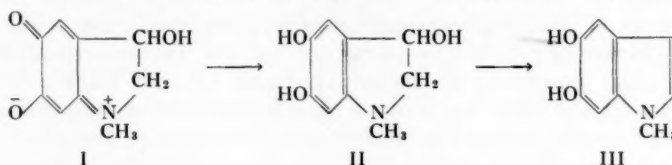
One of the main difficulties encountered in carrying out paper chromatographic studies with the 5,6-dihydroxyindoles is the ease with which they undergo destructive oxidation to melanitic pigments, especially under alkaline conditions; consequently basic solvent systems, including the isopropanol/aqueous ammonia systems widely favored for indole chromatography, are quite useless with this group of indole derivatives. In an investigation of the reduction of adrenochrome with various reducing agents, carried out in these laboratories (7, 8, 9), we have made extensive use of paper chromatographic procedures in the examination of the reaction products. Many of the products encountered in this program were either 5,6-dihydroxyindoles or their derivatives, and one of the most satisfactory systems for the study of these reaction mixtures was found to be 2% acetic acid in water using chromatographic paper that had been extensively prewashed with the running solvent, prior to use. The possible use of *n*-butanol/acetic acid/water (6:1:2) as the running solvent was also considered but it gave somewhat less satisfactory results than 2% acetic acid. In parallel studies on the relatively unstable aminochromes derived

<sup>1</sup>Manuscript received August 8, 1960.

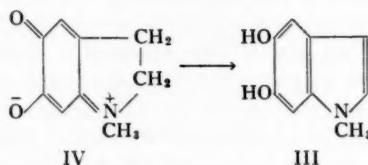
Contribution from the Psychiatric Research Unit, University Hospital, Saskatoon, Saskatchewan. This investigation was supported by grants from the Government of Saskatchewan, the Department of National Health and Welfare (Ottawa), and the Rockefeller Foundation.

from "DOPA", dopamine and noradrenaline, Bouchilloux and Kodja utilized paper chromatographic and paper electrophoretic procedures to investigate both the spontaneous transformations these compounds undergo in aqueous solution and their behavior with reducing agents, using distilled water and *n*-butanol/acetic acid/water as running solvents (10, 11, 12). These authors stress the need to work with well-washed paper to ensure that all traces of sulphites, which can form addition compounds with the 5,6-dihydroxyindoles and the aminochromes have been removed from the chromatographic paper before use.

5,6-Dihydroxyindoles can arise from the aminochromes in at least two ways. If the aminochrome is of the type with a 3-hydroxyl group, reduction leads initially to the formation of an unstable leuco compound, which immediately loses water to form the 5,6-dihydroxyindole (e.g. adrenochrome (I) would be initially reduced to "leuco-adrenochrome" (II) which apparently only has a transient existence and loses water forming 5,6-dihydroxy-*N*-methylinole (III) (see (4) for references)). However, the aminochromes



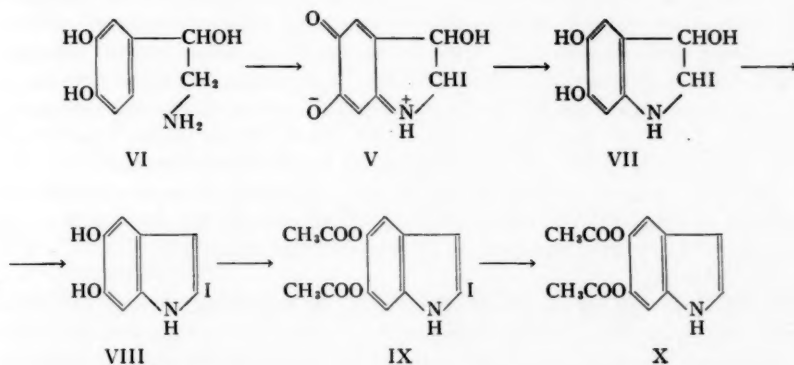
with no 3-hydroxyl substituent undergo an internal oxidation-reduction reaction with considerable ease resulting in the formation of a 5,6-dihydroxyindole. This reaction is catalyzed by  $\text{OH}^-$  and  $\text{Zn}^{++}$  ions, but will also occur spontaneously even in the solid state (e.g. epinochrome (IV) readily rearranges to 5,6-dihydroxy-*N*-methylinole (III)). (See (4) for references.)



The 5,6-dihydroxyindoles used in this investigation were, with the exception of 5,6-dihydroxyindole itself (which was prepared by the method of Beer *et al.* (13)), prepared by the reduction of the corresponding aminochrome. 5,6-Dihydroxy-*N*-methylinole had previously been obtained in about 30% yield from either the hydrogenation of, or the sodium hydrosulphite reduction of, adrenochrome, adrenolutin being obtained as a by-product in each case (14). It was observed, as a result of a preliminary paper chromatographic examination of the reduction mixtures obtained from adrenochrome with a variety of reducing agents, that sodium hydrosulphite always gave the sodium bisulphite addition compound of adrenochrome and smaller amounts of a second water-soluble indole as well as 5,6-dihydroxy-*N*-methylinole (8). However, chromatograms of the zinc and 2% acetic acid, hydrogen sulphide, or sodium borohydride reduction products of adrenochrome showed 5,6-dihydroxy-*N*-methylinole as a very intense spot and only one other relatively weak spot due to an unidentified by-product in each case (8). Contamination of the product with sulphur was a serious disadvantage which was encountered during the use of hydrogen sulphide as the reducing agent for a preparative procedure,

but either zinc and 2% acetic acid or sodium borohydride have proved very satisfactory for the preparation of 5,6-dihydroxy-*N*-methylindole and yields of up to ca. 70% have been obtained from adrenochrome. Attempts to prepare crystalline *N*-ethyl-5,6-dihydroxyindole or 5,6-dihydroxy-*N*-isopropylindole by adaptation of the procedures used for the preparation of 5,6-dihydroxy-*N*-methylindole have, as yet, been unsuccessful, the products being obtained as colorless gums. However, crystalline diacetyl derivatives have been prepared from both the dihydroxy compounds. Etheral solutions of *N*-ethyl-5,6-dihydroxyindole and 5,6-dihydroxy-*N*-isopropylindole (suitable for examination of their paper chromatographic behavior) can be obtained easily by ether extraction of the products obtained from the reduction of *N*-ethylnoradrenochrome and *N*-isopropyl-noradrenochrome respectively. (The reduction can be conveniently carried out with zinc and 2% acetic acid, sodium borohydride, or sodium hydrosulphite.) A simple method has been developed for the preparation of the diacetyl derivatives of 5,6-dihydroxy-*N*-methylindole, *N*-ethyl-5,6-dihydroxyindole, and 5,6-dihydroxy-*N*-isopropylindole, directly from the corresponding catecholamine. The catecholamine is oxidized with silver oxide; the resulting aminochrome solution reduced with zinc and dilute acetic acid (or sodium borohydride) and the crude *N*-alkyl-5,6-dihydroxyindole solution acetylated directly with acetic anhydride in aqueous alkali.

The preparation of 2-iodonoradrenochrome (V) by the oxidation of noradrenaline (VI) with potassium iodate had been reported by Bu'Lock and Harley-Mason but only a relatively low yield of crystalline product was obtained after discarding much tarry material (15). In view of the success of the dilute solution technique, first described by Sobotka and Austin for the preparation of 2-iodoadrenochrome (16) and subsequently used for the preparation of the *N*-ethyl and *N*-isopropyl analogues (17), an attempt was made to prepare 2-iodonoradrenochrome (V) this way. Although a deep-violet solution was obtained, no precipitation of the desired aminochrome occurred, even on standing at 0° for 24 hours, presumably due to its higher water solubility. However, the deep-violet color of the solution was rapidly discharged by the addition of excess ascorbic acid and



5,6-dihydroxy-2-iodoindole (VIII) could be extracted from the reaction mixture with ether; VIII had presumably arisen from the spontaneous dehydration of the initial "leuco" derivative, 2,3-dihydro-3,5,6-trihydroxy-2-iodoindole (VII). In fact, there are several other water-soluble indoles produced in this reaction; this will be discussed in more detail in a later publication (18). 5,6-Diacetoxy-2-iodoindole (IX) could be obtained

from the dihydroxy compound (VIII) by acetylation with acetic anhydride and pyridine. 5,6-Diacetoxyindole (X) was obtained by the deiodination of 5,6-diacetoxy-2-iodoindole with zinc and acetic acid using the procedure described by Bu'Lock and Harley-Mason for the deiodination of several 5,6-di- and 3,5,6-triacetoxyiodoindoles (15). 5,6-Dihydroxy-2-iodo-*N*-methylindole was obtained in crystalline form from 2-iodoadrenochrome by reduction with sodium hydrosulphite (cf. 19) (acetylation with acetic anhydride in pyridine readily gave 5,6-diacetoxy-2-iodo-*N*-methylindole (19)). Reduction of the *N*-ethyl and *N*-isopropyl analogues with sodium hydrosulphite gave *N*-ethyl-5,6-dihydroxy-2-iodoindole and 5,6-dihydroxy-2-iodo-*N*-isopropylindole, respectively; as yet, both of these substances have only been obtained as amorphous solids, but their crystalline diacetyl derivatives have been described (17).

The 5,6-dihydroxyindoles can be very easily detected by color reactions; these highly reactive compounds possess the indole ring system and consequently give colors with the conventional indole reagents such as Ehrlich's reagent, cinnamaldehyde, *p*-dimethylaminocinnamaldehyde, the Hopkins-Cole reagent, and terephthalaldehyde. They also contain phenolic hydroxyl groups and give colored products with many phenol-detecting reagents such as diazotized *p*-nitroaniline, Gibb's reagent, ferric chloride, and Folin and Ciocalteu's reagent. The 5,6-dihydroxyindoles are also catechol derivatives and have strong reducing properties and will reduce such reagents as ammoniacal silver nitrate and ferric chloride/potassium ferricyanide; the 5,6-dihydroxyindoles undergo air oxidation with extreme ease, under alkaline conditions, and spraying with dilute aqueous alkali or even exposing the papers to ammonia fumes converts the compound into a dark insoluble melanin-like pigment. The colors obtained with several chromogenic reagents are given in Table I. In the 5,6-diacetoxyindoles the catechol function is blocked and consequently these compounds are not so readily oxidized as the free hydroxy compounds, nevertheless, they do give colors with most of the usual indole and phenol reagents. The results obtained with several chromogenic reagents are given in Table III.

In view of the success attending the use of 2% acetic acid in water, on acid-washed paper, as a medium for preliminary paper chromatographic studies of the crude reaction mixtures, containing several 5,6-dihydroxyindoles and their derivatives, obtained by reduction of the aminochromes (cf. 7, 8, 9, 19), the  $R_f$  values of several standard 5,6-dihydroxyindoles on acid-washed Whatman No. 1 paper, using 2% acetic acid as running solvent, were determined both by the descending and circular techniques (the results are given in Table II). It will be seen that, in general, the  $R_f$  values obtained by the circular procedure are somewhat higher than those obtained by the descending method. *n*-Butanol/acetic acid/water solvent mixtures have also been employed for paper chromatographic investigations in this field (7, 10, 11, 12) and consequently the  $R_f$  values of several 5,6-dihydroxyindoles were determined in *n*-butanol/acetic acid/water (6:1:2). The results are given in Table II.

Acetic acid (2%) cannot be used satisfactorily as a running solvent for the paper chromatography of the 5,6-diacetoxyindoles owing to their low water solubility; *n*-butanol/acetic acid/water systems are of little value either since the diacetoxy compounds run almost to the solvent front in this solvent. A method for studying the paper chromatographic behavior of steroids was introduced about 10 years ago (20, 21) which used a highly polar stationary phase (e.g. paper treated with formamide or propylene glycol) and a non-polar mobile phase (e.g. cyclohexane, benzene, chloroform, etc.); this type of system has subsequently been widely used for the chromatographic separation of the ergot alkaloids (22, 23, 24). This technique has now been extended successfully to include



the 5,6-diacetoxyindoles which can be easily separated on formamide-treated paper (the "pH" of the formamide was adjusted to 5 by the cautious addition of 98% formic acid prior to impregnation of the paper) using non-polar running solvents, such as: light petroleum, cyclohexane, benzene/light petroleum (1:9), carbon tetrachloride, etc. Benzene gave satisfactory  $R_f$ 's with the 5,6-diacetoxyindoles not alkylated on the nitrogen atom; however, the *N*-alkyl derivatives ran almost to the solvent front. The results obtained are given in Table V. It was possible to utilize this general procedure for a study of the paper chromatography of the 5,6-dihydroxyindoles, although it was necessary to use a slightly more polar mobile phase: i.e. benzene/chloroform (1:1), chloroform, benzene/ethyl acetate (3:1), chloroform/ethyl acetate (4:1), and dichloromethane. With these solvent systems satisfactory  $R_f$  values could be obtained for all the dihydroxy compounds studied; the results obtained are given in Table IV. The "pH" of the formamide was adjusted to 5, prior to impregnation of the paper, in all cases, since air oxidation of the 5,6-dihydroxyindoles was slower, under weakly acid, than neutral or alkaline conditions. Some experiments were carried out with the "pH" of the formamide adjusted to 7 or 9 before treatment of the paper, but in both cases, particularly the latter, considerable dark streaking behind the 5,6-dihydroxyindole spots was observed, presumably due to melanin formation. Changing the "pH" of the stationary phase also alters the  $R_f$ 's of the compounds but only relatively few runs were carried out and will not be reported here. Throughout these investigations involving the use of formamide-treated paper it was desirable to saturate the mobile phase with formamide; however, with the chlorinated solvents, particularly dichloromethane it was found that it was better, in practice, to add slightly less than the amount of formamide required to saturate the solvent so as to ensure that the formamide remains in solution during the running of the chromatograms. If the solvents become cloudy due to separation of free formamide, inconsistent and unsatisfactory results are obtained. Gröger used the formamide/dichloromethane system to separate the Clavin group of ergot alkaloids and stressed that the mobile phase must not be allowed to become cloudy during the development of the chromatograms (25). During the course of these investigations the authors became aware of a paper by Prochazka *et al.* on the paper chromatography of indoles in general and the  $R_f$ 's of several indoles on formamide-treated paper with cyclohexane, benzene, and chloroform as the mobile phases were reported (26); however, no 5,6-dihydroxyindoles or 5,6-diacetoxyindoles were included in the group of substances studied.

## EXPERIMENTAL

### CHEMICAL

#### (I) 5,6-Dihydroxyindoles

##### (A) 5,6-Dihydroxyindole

5,6-Dihydroxyindole was prepared by the method of Beer, Clarke, Khorana, and Robertson (13).

##### (B) 5,6-Dihydroxy-N-methylindole

(i) *From adrenochrome.*—(a) A solution of adrenochrome (1.0 g) in water (100 ml) was added slowly, with stirring, to a solution of sodium borohydride (0.3 g) in water (25 ml); the red color of the adrenochrome solution was instantly discharged and a pale yellow solution obtained. After decomposition of excess reducing agent by the cautious dropwise addition of 2 *N* sulphuric acid, the reaction mixture was extracted with peroxide-free ether (4×100 ml). The combined, dried ( $\text{Na}_2\text{SO}_4$ ) extracts were concentrated to small



bulk, under nitrogen, below 30°; dry benzene (100 ml) was added and the remaining ether distilled off. (It was found that if the original ethereal solution was evaporated to dryness, the residue would not completely redissolve in benzene.) The product was adsorbed on a silica gel\* column (10×2.4 cm); elution of the column with benzene (150 ml) and benzene/ethyl acetate (95:5) (300 ml) gave white solids (the solvent having been removed *in vacuo*, under nitrogen, below 30°), which on recrystallization from light petroleum (b.p. 100–120°) gave 5,6-dihydroxy-*N*-methyldole (0.68 g) as colorless needles (m.p. 134–135°). (Found: C, 66.14; H, 5.58.  $C_9H_9NO_2$  requires C, 66.25; H, 5.56%.) The melting point of this substance is quoted in the literature as 136° (14) and 133° (27).† (b) Zinc dust (40.0 g) was added, with vigorous stirring, to a solution of adrenochrome (1.0 g) in 2% acetic acid (200 ml). The red color of the solution was rapidly discharged and stirring was maintained for a further 4 to 5 minutes. The reaction mixture was filtered (suction) and both the residue and filtrate repeatedly extracted with peroxide-free ether. The combined, dried ( $Na_2SO_4$ ) ethereal extracts were concentrated and the product worked up and purified chromatographically as described above (see Subsection i(a) above). 5,6-Dihydroxy-*N*-methyldole (0.35 g) was obtained in colorless needles (m.p. 133–134°).

(ii) *From adrenaline*.—Silver oxide (10 g) was added to a well-stirred solution of adrenaline bitartrate (2.5 g) in water (50 ml). The reaction mixture was vigorously stirred, with external cooling, for a further 3 minutes after which time the resulting deep-red suspension was filtered (with suction) through a Dowex-1( $Cl^-$ ) resin bed (3.5×1.5 cm‡) directly into a vigorously stirred solution of sodium borohydride (0.6 g) in water (25 ml). (It was necessary to add a few drops of peroxide-free ether from time to time to control the vigorous frothing that occurred.) Sulphuric acid (2 *N*) was added dropwise to decompose the excess sodium borohydride and the solution was immediately extracted with peroxide-free ether (4×125 ml). The combined, dried ( $Na_2SO_4$ ) extracts were concentrated and the products were worked up and purified chromatographically, as described in Subsection i(a) above, to give 5,6-dihydroxy-*N*-methyldole in colorless needles (0.37 g), m.p. 133–134°.

(C) *N*-Ethyl-5,6-dihydroxyindole

*N*-Ethyl-5,6-dihydroxyindole was prepared in solution in peroxide-free ether. As yet, *N*-ethyl-5,6-dihydroxyindole has only been obtained as a yellow gum, however, a crystalline diacetyl derivative has been prepared (see Section II(C)). Sodium hydrosulphite (50 mg) was added to a solution of *N*-ethylnoradrenochrome (20 mg, prepared by the method of Heacock and Scott (17)) in water (10 ml); the red color of the solution was rapidly discharged and the reaction mixture extracted with peroxide-free ether (2×4 ml). The dried ( $Na_2SO_4$ ) ethereal extract containing the *N*-ethyl-5,6-dihydroxyindole (concentration, ca. 1 mg/ml) was used directly for the chromatographic studies.

(D) 5,6-Dihydroxy-*N*-isopropylindole

5,6-Dihydroxy-*N*-isopropylindole was prepared in solution in peroxide-free ether (at a concentration of ca. 1 mg/ml) from *N*-isopropylnoradrenochrome (17) in an analogous manner to the method described above for the preparation of the *N*-ethyl derivative. As in the case of the *N*-ethyl analogue, 5,6-dihydroxy-*N*-isopropylindole has, as yet, only

\*In this and subsequent experiments described in this paper the chromatographic silica gel used was obtained from L. Light & Co. (200/300 mesh size).

†In this case the substance was prepared by the rearrangement of epinochrome.

‡The resin (200/400 mesh size) was purified by extensive washing with: (a) 2 *N* hydrochloric acid and (b) water until neutral to litmus. This procedure was used for the preparation of the resin beds described throughout this paper.

been obtained as a yellow gum, but a crystalline diacetyl derivative has been prepared (see Section II(D)).

(E) *5,6-Dihydroxy-2-iodoindole*

Potassium iodate (3.2 g) was added to a solution of noradrenaline hydrochloride (2.0 g) in water (1600 ml) and the reaction mixture was stirred at room temperature for 2 hours. An excess of solid ascorbic acid was added (until the deep-violet color of the solution was discharged) and the reaction mixture extracted with peroxide-free ether (5×200 ml). Dry benzene (250 ml) was added to the dried ( $\text{Na}_2\text{SO}_4$ ) ethereal extract and the ether was removed *in vacuo*, under nitrogen (bath temperature below 30°); the final traces of ether were removed by the addition of further small quantities of dry benzene and removal of them *in vacuo*. (If the ether extract was concentrated to dryness without the prior addition of benzene, the dark residue obtained was only partially soluble in benzene.) The crude product (obtained in solution in benzene by the method described above) gave 5,6-dihydroxy-2-iodoindole (1.1 g), m.p. 108–108.5° (with decomposition), in pale yellow needles after chromatographic purification on a silica gel column (7×2.4 cm) (adsorption from benzene – light petroleum (b.p. 80–100°) (1:1) and elution with this solvent and benzene). (Found: C, 35.05; H, 2.21; I, 45.93.  $\text{C}_8\text{H}_6\text{NO}_2\text{I}$  requires C, 34.94; H, 2.20; I, 46.14%.) This product was relatively unstable and decomposed to a black vitreous substance on standing 4 weeks at room temperature.

(F) *5,6-Dihydroxy-2-iodo-N-methylindole*

5,6-Dihydroxy-2-iodo-N-methylindole was prepared in the manner described by Heacock and Scott (19).

(G) *N-Ethyl-5,6-dihydroxy-2-iodoindole*

N-Ethyl-5,6-dihydroxy-2-iodoindole was prepared in solution in peroxide-free ether; although, as yet, N-ethyl-5,6-dihydroxy-2-iodoindole has only been obtained as a brownish-yellow amorphous solid, a crystalline diacetyl derivative has been described (17). Sodium hydrosulphite (50 mg) was added to a stirred suspension of N-ethyl-2-iodonoradrenochrome (30 mg, prepared by the method of Heacock and Scott (17)) in water (10 ml). After being stirred for ca. 2 minutes the cloudy yellow suspension was filtered from residual solid material and the filtrate was extracted with peroxide-free ether (4×4 ml). The dried ( $\text{Na}_2\text{SO}_4$ ) ethereal extract containing the N-ethyl-5,6-dihydroxy-2-iodoindole (concentration, ca. 1 mg/ml) was used directly for the chromatographic studies.

(H) *5,6-Dihydroxy-2-iodo-N-isopropylindole*

5,6-Dihydroxy-2-iodo-N-isopropylindole was prepared in peroxide-free ether solution (from 2-iodo-N-isopropylnoradrenochrome (17)) at a concentration of ca. 1 mg/ml in an analogous manner to that described above for the N-ethyl derivative. As yet, 5,6-dihydroxy-2-iodo-N-isopropylindole has only been obtained as a greenish-brown amorphous solid but a crystalline diacetyl derivative has been described (17).

(I) *2-Bromo-5,6-dihydroxy-N-methylindole*

2-Bromo-5,6-dihydroxy-N-methylindole was prepared by the method described by Harley-Mason (14).

(II) *5,6-Diacetoxyindoles*

(A) *5,6-Diacetoxyindole*

Zinc powder (6.0 g) was added portionwise, during a period of 15 minutes, to a solution of 5,6-diacetoxy-2-iodoindole (0.9 g, prepared by the method described below (Section II

(E)) in glacial acetic acid (12 ml). The reaction mixture was filtered and the residual zinc was washed with glacial acetic acid (3×5 ml); the combined filtrate and washings were poured into ice water. The aqueous reaction mixture was extracted with peroxide-free ether (5×150 ml) and the ethereal extract washed free of acetic acid with saturated aqueous sodium bicarbonate. Concentration (*in vacuo*), of the dried ( $\text{Na}_2\text{SO}_4$ ) ethereal extract, gave a red-brown gum, which by chromatographic purification on a short silica gel column using benzene as eluent and recrystallization from light petroleum (b.p. 80–100°) gave 5,6-diacetoxyindole in colorless needles (0.1 g), m.p. 139–140°. (Found: C, 61.77; H, 4.71.  $\text{C}_{12}\text{H}_{11}\text{NO}_4$  requires C, 61.80; H, 4.75%.) Beer *et al.* (13), who prepared this compound by a different route report a melting point of 130–133°.

(B) 5,6-Diacetoxy-N-methylindole

(i) Adrenaline (1.6 g) was suspended in water (50 ml) and concentrated hydrochloric acid was added dropwise until a clear solution was obtained. Silver oxide (8 g) was added to the stirred solution, and the stirring continued for a further 3 minutes. The reaction mixture was filtered (with suction) through a Dowex-1 ( $\text{Cl}^-$ ) resin bed (1.5×2.5 cm) directly into a stirred solution of sodium borohydride (0.6 g) in water (25 ml). (The addition of a few drops of peroxide-free ether was necessary at this stage to control the vigorous frothing that occurred.) The excess reducing agent was decomposed by the addition of glacial acetic acid (3 ml). A rapid stream of nitrogen was passed through the stirred solution, cooled to ca. 10–15°, and 40% aqueous sodium hydroxide (10 ml) was added, followed directly by acetic anhydride (5 ml). After being stirred at room temperature for 30 minutes (the cooling bath was removed after 5 minutes), the reaction mixture was extracted with peroxide-free ether (5×100 ml). The combined ethereal extracts were washed with 5% aqueous sodium bicarbonate (2×100 ml) and water (100 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated to dryness (*in vacuo*, below 40°). The product, a greenish-brown gum, was dissolved in benzene – light petroleum (b.p. 80–100°) (1:1) and adsorbed on a silica gel column (12.5×2.4 cm). Elution of the column with the same solvent (100 ml) gave a small quantity of a pale-yellow gum which was discarded; further elution with benzene (400 ml) gave a white solid which on recrystallization from light petroleum (b.p. 80–100°) gave 5,6-diacetoxy-N-methylindole (0.69 g), m.p. 109–110°. (Found: C, 63.10; H, 5.24; N, 5.56.  $\text{C}_{13}\text{H}_{13}\text{NO}_4$  requires C, 63.15; H, 5.30; N, 5.66%.) This melting point is somewhat higher than those previously quoted in the literature: 101–102° (27), 101° (28), and 104–105° (14). (The product obtained above did not depress the melting point of a sample prepared by direct acetylation of crystalline 5,6-dihydroxy-N-methylindole with acetic anhydride in pyridine.)

(ii) Adrenaline (1.6 g) was suspended in water (40 ml) and concentrated hydrochloric acid added dropwise until a clear solution was obtained. Silver oxide (8.0 g) was added to the stirred solution and the stirring continued for 3 minutes and the reaction mixture was filtered through a Dowex-1 ( $\text{Cl}^-$ ) resin bed (1.5×2.5 cm). Glacial acetic acid (2 ml) was added to the vigorously stirred filtrate followed by zinc powder (40.0 g), which caused a rapid discharge of the red color. The product was filtered; the zinc residue was washed with acetone (3×5 ml), and the washings were added to the filtrate. The solution of crude 5,6-dihydroxy-N-methylindole so obtained was acetylated directly and the products worked up and purified chromatographically by the methods described above (Subsection B(i)) giving 5,6-diacetoxy-N-methylindole (0.42 g), m.p. 109.5–110.5°.

(C) 5,6-Diacetoxy-N-ethylindole

N-Ethylnoradrenaline (1.6 g) was suspended in water (40 ml) and concentrated

hydrochloric acid was added dropwise until a clear solution was obtained; silver oxide (8.0 g) was added to the stirred solution and stirring continued for 3 minutes; the product was filtered through a Dowex-1 ( $\text{Cl}^-$ ) resin bed ( $1.5 \times 2.5$  cm) and glacial acetic acid (2 ml), followed by zinc powder (40 g), added to the stirred filtrate. The reaction mixture was filtered; the residual zinc was washed with acetone ( $3 \times 5$  ml); and the washings were added to the filtrate. A rapid stream of nitrogen was passed through the stirred filtrate, cooled to ca.  $10-15^\circ$ , and 40% sodium hydroxide (10 ml) was added, followed directly by acetic anhydride (5 ml). After stirring at room temperature for 30 minutes (the cooling bath was removed after about 5 minutes), the reaction mixture was extracted with peroxide-free ether ( $5 \times 100$  ml). The combined ethereal extracts were washed with 5% aqueous sodium bicarbonate ( $2 \times 100$  ml) and water (100 ml). Concentration, *in vacuo*, below  $40^\circ$ , of the dried ( $\text{Na}_2\text{SO}_4$ ) extract, afforded a greenish-brown gum which was dissolved in benzene - light petroleum (b.p.  $80-100^\circ$ ) (1:1) and adsorbed on a silica gel column ( $12.5 \times 2.4$  cm). Elution of the column with this solvent (100 ml) gave a trace of gum which was rejected; further elution with benzene (500 ml) gave a white crystalline solid which yielded 5,6-diacetoxy-*N*-ethylindole (0.5 g), m.p.  $107-108.5^\circ$ , on recrystallization from light petroleum (b.p.  $80-100^\circ$ ). (Found: C, 64.52; H, 5.78; N, 5.14.  $\text{C}_{14}\text{H}_{15}\text{NO}_4$  requires C, 64.37; H, 5.79; N, 5.36%.)

(D) 5,6-Diacetoxy-*N*-isopropylindole

(i) Silver oxide (16 g) was added to a solution of *N*-isopropylnoradrenaline hydrochloride (4 g) in water (80 ml) and the suspension vigorously stirred for 2 to 3 minutes. The reaction mixture was filtered through a Dowex-1 ( $\text{Cl}^-$ ) resin bed ( $2.5 \times 1.5$  cm) directly into a cooled stirred solution of sodium borohydride (0.75 g) in water (20 ml). (Excessive foaming at this stage was controlled by the addition of small quantities of peroxide-free ether.) The reaction mixture was acidified with glacial acetic acid (3 ml), and a rapid stream of nitrogen passed through the solution, cooled to ca.  $10-15^\circ$ . Aqueous sodium hydroxide (40%, 20 ml) was added, followed directly by acetic anhydride (10 ml). After being stirred at room temperature for 30 minutes (the cooling bath was removed after 5 minutes), the reaction mixture was extracted with peroxide-free ether ( $5 \times 100$  ml); the combined ethereal extracts were washed with 5% aqueous sodium bicarbonate ( $2 \times 50$  ml) and water (100 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated to dryness *in vacuo*, below  $40^\circ$ . The product was dissolved in benzene - light petroleum (b.p.  $80-100^\circ$ ) (1:1) and adsorbed on a silica gel column ( $12.5 \times 2.4$  cm). Elution of the column with this solvent (150 ml) gave only traces of gums which were rejected, further elution with benzene (450 ml) gave a white solid, which on recrystallization from benzene - light petroleum (b.p.  $80-100^\circ$ ), gave 5,6-diacetoxy-*N*-isopropylindole as colorless prisms (0.5 g), m.p.  $90.5-91^\circ$ . (Found: C, 65.60; H, 6.15; N, 4.94.  $\text{C}_{15}\text{H}_{17}\text{NO}_4$  requires C, 65.43; H, 6.23; N, 5.09%.)

(ii) A solution of *N*-isopropylnoradrenochrome (from 2 g of *N*-isopropylnoradrenaline sulphate) in water (40 ml) prepared by the method described above was acidified with glacial acetic acid (5 ml) and reduced with zinc powder (40 g). The reaction product was acetylated directly with acetic anhydride (5 ml) in the presence of 40% aqueous sodium hydroxide (10 ml) by the method previously described. The product was extracted and purified chromatographically by the above method and 5,6-diacetoxy-*N*-isopropylnoradrenochrome was obtained in colorless elongated prisms (0.75 g), m.p.  $89.5-90.5^\circ$ .

(E) 5,6-Diacetoxy-2-iodoindole

An ethereal solution of crude 5,6-dihydroxy-2-iodoindole was prepared by the method



described in Section I(E). A mixture of acetic anhydride (15 ml) and dry\* pyridine (15 ml) was added and the ether removed *in vacuo*, under nitrogen (bath temperature below 40°). The residual acetylation mixture was allowed to stand overnight at room temperature, after which time it was poured, with stirring, into an ice-water mixture. A brown oil separated, which did not solidify. The product was extracted with peroxide-free ether (5×150 ml) and the ethereal extract washed free of acetic acid with saturated aqueous sodium bicarbonate. Concentration of the dried (Na<sub>2</sub>SO<sub>4</sub>) ethereal extract gave a brownish residue which was dissolved in a mixture of benzene and light petroleum (b.p. 80–100°) (1:1) and purified chromatographically on a short silica gel column, the same solvent being used for elution. 5,6-Diacetoxy-2-iodoindole (1.1 g), m.p. 125–126.5°, was obtained in fluffy white needles. (Found: C, 40.02; H, 2.77; I, 35.30. C<sub>12</sub>H<sub>10</sub>NO<sub>4</sub>I requires C, 40.15; H, 2.81; I, 35.35%.)

(F) *5,6-Diacetoxy-N-methyl-2-iodoindole*

5,6-Diacetoxy-*N*-methyl-2-iodoindole was prepared by the method of Heacock and Scott (19).

(G) *5,6-Diacetoxy-N-ethyl-2-iodoindole*

5,6-Diacetoxy-*N*-ethyl-2-iodoindole was prepared in the manner described by Heacock and Scott (17).

(H) *5,6-Diacetoxy-2-iodo-N-isopropylindole*

5,6-Diacetoxy-2-iodo-*N*-isopropylindole was prepared in the manner described by Heacock and Scott (17).

#### CHROMOGENIC REAGENTS

(a) *Ehrlich's reagent*.—*p*-Dimethylaminobenzaldehyde (1 g) was dissolved in a mixture of concentrated hydrochloric acid (30 ml) and ethanol (30 ml) and the solution was diluted to 100 ml with water.

(b) *Cinnamaldehyde solution* (cf. Sen and Leopold (29)).—Cinnamaldehyde (5 ml) was dissolved in a mixture of ethanol (95 ml) and concentrated hydrochloric acid (5 ml).

(c) *p*-Dimethylaminocinnamaldehyde solution (cf. Harley-Mason and Archer (30)).—*p*-Dimethylaminocinnamaldehyde (2 g) was dissolved in 6 *N* hydrochloric acid (100 ml) and ethanol (100 ml). The stock solution (10 ml) was diluted with ethanol (40 ml) prior to use.

(d) *Hopkins-Cole reagent* (cf. Benedict (31)).—A saturated aqueous solution of oxalic acid (250 ml) was added slowly to a cooled suspension of magnesium filings (10 g) in sufficient water to just cover the metal. After addition of the acid the flask was vigorously shaken for a few minutes and the solution filtered. The filtrate was stabilized by the addition of a little glacial acetic acid and diluted to 1000 ml with water.

(e) *Acidic oxidizing reagent* (cf. Jepson (32), p. 125).—Freshly prepared saturated potassium persulphate solution (1 ml†) was mixed with concentrated hydrochloric acid (10 ml) and acetone (40 ml), and the solution used immediately.

(f) *Salkowski reagent* (cf. Sen and Leopold (29)).—Ferric chloride (0.5 *M*, 2 ml) was added to 5% perchloric acid (100 ml).

(g) *Terephthalaldehyde solution* (cf. Curzon and Giltrow (33)).—Terephthalaldehyde (0.2 g) was dissolved in a mixture of acetone (90 ml) and acetic acid (10 ml). After being

\*Distilled from phosphorus pentoxide.

†This quantity of potassium persulphate solution is greater than that used by Jepson and gives more intense colors in the cases studied. The use of the stronger reagent was suggested to the authors by Dr. F. Wightman of Carleton University, Ottawa.



sprayed with this solution the chromatograms were sprayed with 2% concentrated hydrochloric acid in acetone.

(h) *Nitrose reagent* (cf. Jepson (32), p. 127).—Sodium nitrite (1 ml of a 5% aqueous solution) was added to a solution of concentrated nitric acid (5 ml) in acetone (45 ml) and the mixture was used directly.

(i) *Formaldehyde/hydrochloric acid* (cf. Prochazka *et al.* (26)).—Aqueous formaldehyde solution (10 ml of a 30 to 40% solution) was mixed with concentrated hydrochloric acid (10 ml) and water (20 ml). In order to develop the colors, the chromatograms were warmed to 90–95° after spraying.

(j) *Xanthydrol reagent* (cf. Dickmann and Crockett (34)).—Xanthydrol (0.2 g) was dissolved in ethanol (90 ml) and concentrated hydrochloric acid (10 ml).

(k) *Gibb's reagent*.—*N*-2,6-Trichloro-*p*-quinoneimine (2 g) was dissolved in ethanol (100 ml).

(l) *Diazotized p-nitroaniline* (cf. Bray *et al.* (35)).—A *p*-nitroaniline solution (25 ml) of a 0.3% solution in 8% (w/v) hydrochloric acid was diazotized with sodium nitrite solution (1.5 ml of a 5% solution) immediately prior to use. (The second spraying with aqueous alkali was omitted.)

(m) *Folin and Ciocalteu's reagent*.—This solution was available commercially (B. D. H.) and was diluted with two volumes of water prior to use.

(n) *Sodium molybdate/hydrochloric acid* (cf. Coulson and Evans (36)).—Sodium molybdate solution (10%, 20 ml) was diluted with 0.5 *N* hydrochloric acid (10 ml).

(o) *Ferric chloride/potassium ferricyanide reagent* (as described by Heacock *et al.* (37)).—Ferric chloride (3%, 5 ml) and potassium ferricyanide (3%, 5 ml) were mixed immediately prior to use and the solution was diluted to 100 ml with water. In order to prevent discoloration of the papers after spraying with this reagent, they were subsequently washed with (a) water, (b) 2 *N* hydrochloric acid, and (c) water.

(p) *Ferric chloride solution*.—Ferric chloride (3 g) was dissolved in water (100 ml) containing a few drops of hydrochloric acid.

(q) *Ammoniacal silver nitrate*.—Ammonia solution (5 *N*) was added dropwise to 0.1 *N* aqueous silver nitrate, until the precipitate which initially formed just redissolved.

#### CHROMATOGRAPHIC PROCEDURE (5,6-DIHYDROXYINDOLES)

##### (A) *Descending*

1. *Paper*.—Whatman No. 1 paper was washed with 2% acetic acid for 48 hours and dried prior to use.

2. *Solvents*.—*S*<sub>1</sub>, 2% acetic acid in water; *S*<sub>2</sub>, *n*-butanol:glacial acetic acid:water (6:1:2).

3. *Detection*.—All the chromogenic reagents mentioned above give colors with the 5,6-dihydroxyindoles (see Table I). Satisfactory color intensities were obtained with spots derived from 10 to 25  $\mu$ g of the compounds. The unhalogenated 5,6-dihydroxyindoles also show a definite light blue to mauve fluorescence in ultraviolet light.

##### (B) *Circular*

1. *Paper*.—(a) Whatman No. 1 paper, slotted disks (diameter = 26.5 cm\*); (b) disks (diameter = 26.5 cm) of Whatman 3MM paper were dipped into a 30% solution of reagent grade formamide ("pH" = 5)<sup>†</sup> in acetone, removed, blotted dry, and allowed to dry in air for 20 minutes.

\*As supplied by the Shandon Scientific Company Ltd.

<sup>†</sup>The "pH" of the formamide was adjusted to 5 by the careful dropwise addition of 98% formic acid.

Color reactions  
of some 5,6-dihydroxyindoles

5,6-Dihydroxyindole derivative	Code name	R <sub>1</sub>	R <sub>2</sub>	Ehr.	Cin.	DMCA	H.C.†	TPA‡	FH
5,6-Dihydroxyindole	DHI	H	H	BV → GyG	OrB → RBr	GyG → BG	P	OG	G → B
5,6-Dihydroxy-N-methylindole	DHMI	CH <sub>3</sub>	H	BV	OrBr → VBr	BG → B	PV	OG	YG →
N-Ethyl-5,6-dihydroxyindole	DHEI	C <sub>2</sub> H <sub>5</sub>	H	BV	OrBr → VBr	BG → B	PV	OG	YG →
5,6-Dihydroxy-N-isopropylindole	DHPrI	i-C <sub>3</sub> H <sub>7</sub>	H	BV → V	OrBr → VBr	BG → BGy	PV	GyV	Y → G
5,6-Dihydroxy-2-iodoindole	IodoDHI	H	I	BV → GyG	RP → Br	B → BG	Gy → GyP	Br → GyB	OG →
5,6-Dihydroxy-2-iodo-N-methylindole	IodoDHMI	CH <sub>3</sub>	I	BV	RP → VBr	BG → B	V	GyV	OG →
N-Ethyl-5,6-dihydroxy-2-iodoindole	IodoDHEI	C <sub>2</sub> H <sub>5</sub>	I	BV	RP → VBr	BG → B	GyV	GyV	OG →
5,6-Dihydroxy-2-iodo-N-isopropylindole	IodoDHPrI	i-C <sub>3</sub> H <sub>7</sub>	I	BV	RP → GyP	BG → BV	GyV	GyV	BG →
2-Bromo-5,6-dihydroxy-N-methylindole	BromoDHMI	CH <sub>3</sub>	Br	BV	RP → VBr	BG → BGy	GyV	Gy	G → B

\*Initial colors and colors after 24 hours (if significantly different) are given.

†These colors develop slowly.

‡First change occurs rapidly; final change occurs overnight. The initial color changes observed with this reagent are confusing and its use is not recommended.

REAGENTS: Ehr. = Ehrlich's reagent; Cin. = cinnamaldehyde; DMCA = *p*-Dimethylaminocinnamaldehyde; H.C. = Hopkins-Cole reagent; TPA = terephthalaldehyde; FHCl = Formaldehyde/hydrochloric acid reagent; Ac.ox. = Acidic oxidizing reagent; Sal. = Salkowski reagent; nitro = nitro reagent; DPNA = Diazotized *p*-nitroaniline; Gib. = Gibb's reagent;

2. *Solvents*.—S<sub>1</sub>, 2% acetic acid in water; S<sub>3</sub>, chloroform\* (10 ml) and benzene† (10 ml) containing 0.1 ml formamide; S<sub>4</sub>, chloroform\* containing 1.4% formamide; S<sub>5</sub>, ethyl acetate\* (5 ml) and benzene† (15 ml) saturated with formamide; a small quantity of formamide was added to this mixture; the mixture was well shaken, allowed to stand and the clear supernatant layer was decanted and used; S<sub>6</sub>, ethyl acetate\* (4 ml) and chloroform\* (16 ml) containing 0.2 ml formamide; S<sub>7</sub>, dichloromethane\* containing 1.4% formamide.

3. *Apparatus*.—A modified form of the Kawerau circular chromatography apparatus‡ was used. The glass capillary solvent feed supplied with the apparatus was unsatisfactory and was replaced by a cotton yarn wick (1/8 in.). The solvent was contained in a 6-cm petri dish.

4. *Detection*.—(a) Any of the chromogenic reagents described in the previous section could be used to detect the spots when the runs were carried out with 2% acetic acid on untreated paper. (b) With the runs on formamide-treated paper, either fluorescence in ultraviolet light or the colors given with Ehrlich's reagent were used to locate the spots.

#### CHROMATOGRAPHIC PROCEDURE (5,6-DIACETOXYINDOLES)

##### Circular

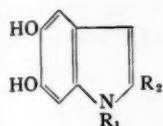
1. *Paper*.—Formamide-treated paper was prepared as described in the previous section.

2. *Solvents*.—S<sub>8</sub>, light petroleum (B.D.H. A.R. grade, b.p. 60–80°); S<sub>9</sub>, cyclohexane,\* S<sub>10</sub>, benzene† (1 ml) mixed with light petroleum (B.D.H. A.R. grade, b.p. 60–80°) (9 ml); S<sub>11</sub>, benzene† (In each of the above cases a small quantity of formamide was added to the

\*Reagent grade.

†Dried over sodium.

‡As supplied by the Shandon Scientific Company Ltd.



Colors\* with chromogenic reagents

	FHCl	Ac.ox.	Sal.	Nitroso	DPNA	Gib.	F. and C.	S.M.	Fe	AmAg	Xan.
G → BGy	Y → YBr	Gy	P → Br → Gy†	M → VBr	Br	Gy → BGy	GyG	Gy	Bl	G → GyG	
YG → BGy	Br → GyBr	Y → Gy	OG → GyBr → YBr‡	M → VBr	Br	Gy → BGy	GyG	Bl	DBr	Gy	
YG → BGy	Br → GyBr	Y → YBr	OG → GyBr → YBr‡	M → VBr	Br	Gy → BGy	GyG	Bl	DBr	GyV → Gy	
Y → Gy	Br → GyBr	Or → GyBr	OG → Y → YBr‡	RB → Br	Br	Gy → BGy	BGy → GyG	Bl	DBr	GyV → Gy	
OG → B	Y → Gy	YBr → Gy	B → GyY → GyBr‡	M → VBr	Br	Gy → BGy	BBl	Gy	Bl	GyV	
OG → B	Y → GyBr	Y → GyBr	B → GyG → GyBr‡	GyM → Br	GyBr → Br	Gy → BGy	GyG	Gy	Br	BG → YG	
OG → B	Y → GyBr	Y → YBr	Br → YBr	GyM → Br	GyV → Br	Gy → BGy	GyG	Gy	Br	B → YG	
BG → Gy	Y → Br	Gy → Br	Br → YBr	GyM → Br	GyV → Br	Gy → BGy	Gy → Br	Gy	Br	B	
G → B	Y → GyY	YGy → GyP	GyP → DBr	GyM → VBr	GyBr → Br	Gy → BGy	BGy → GyG	Gy	DBr	Gy → OG	

F. and C. = Folin and Ciocalteu's reagent; S.M. = sodium molybdate/hydrochloric acid reagent; Fe = ferric chloride; AmAg = ammoniacal silver nitrate; Xan. = xanthidol reagent.

Colors: B = blue; BV = blue-violet; BG = blue-green; BGy = blue-grey; V = violet; VBr = violet-brown; GyV = grey-violet; PV = pink-violet; M = magenta; GyM = grey-magenta; P = pink; OrP = orange-pink; RP = red-pink; GyP = grey-pink; PBr = pink-brown; Br = Brown; DBr = dark brown; OrBr = orange-brown; Or = orange; YBr = yellow-brown; GyBr = grey-brown; BBl = black-brown; Y = yellow; GyY = grey-yellow; YG = yellow-green; G = green; OG = olive green; GyG = grey-green; Gy = grey; Bl = Black; BBl = blue-black.

TABLE II

The  $R_f$  values of some 5,6-dihydroxyindoles on Whatman No. 1 paper

Substance*	Average $R_f$ † in solvent:		
	$S_1$ ‡	$S_1$ §	$S_2$
DHI	40	56	64
DHMI	46	58	76
DHEI	53	65	81
DHPrI	58	71	84
IodoDHI	21	36	77
IodoDHMI	20	29	83
IodoDHEI	25	38	84
IodoDHPrI	27	40	87
BromoDHMI	23	—	79

\*Code names as defined in Table I.

† $R_f \times 100$ .

‡Descending.

§Circular.

||The  $R_f$ 's of DHI, DHMI, IodoDHI, and IodoDHMI have been reported as 65, 79, 83, 89 on unwashed paper with  $n$ -butanol/acetic acid/water (78:5:17) as running solvent (11, 12).

solvent; the mixture was well shaken, allowed to stand and the clear supernatant layer decanted and used.);  $S_{12}$ , carbon tetrachloride\* saturated with formamide. (A few drops of formamide were added to the carbon tetrachloride; the mixture shaken, allowed to stand and the clear lower layer separated and used directly.)

3. *Detection*.—The 5,6-diacetoxyindoles give colors with all the usual indole reagents

\*Reagent grade.

TAB  
The color reactions  
of some 5,6-diacetoxyindoles

5,6-Diacetoxyindole derivative	Code name	R <sub>1</sub>	R <sub>2</sub>	Ehr.	Cin.	DMCA
5,6-Diacetoxyindole	DAI	H	H	PV → BGy	OrP → Br	B → BG
5,6-Diacetoxy-N-methylindole	DAMI	CH <sub>3</sub>	H	PV → BV	OrP → Br	BG → Gy <sup>†</sup>
5,6-Diacetoxy-N-ethylindole	DAEI	C <sub>2</sub> H <sub>5</sub>	H	PV → BV	OrP → Br	BG
5,6-Diacetoxy-N-isopropylindole	DAPrI	i-C <sub>3</sub> H <sub>7</sub>	H	PV → BV	OrP → Br	BG
5,6-Diacetoxy-2-iodoindole	IodoDAI	H	I	PV	P → BV → Y <sup>‡</sup>	B → BG <sup>‡</sup>
5,6-Diacetoxy-2-iodo-N-methylindole	IodoDAMI	CH <sub>3</sub>	I	PV	P → BV → Y <sup>‡</sup>	BG → Gy <sup>‡</sup>
5,6-Diacetoxy-N-ethyl-2-iodoindole	IodoDAEI	C <sub>2</sub> H <sub>5</sub>	I	PV	P → BV → Y <sup>‡</sup>	B → BG <sup>‡</sup>
5,6-Diacetoxy-2-iodo-N-isopropylindole	IodoDAPrI	i-C <sub>3</sub> H <sub>7</sub>	I	PV	P → BV → Y <sup>‡</sup>	B → BG <sup>‡</sup>

\*Initial colors and colors after 24 hours (if significantly different are given).

†The abbreviations for the chromogenic reagents and colors produced are the same as those used in Table I.

‡Initial colors slow to develop.

TABLE IV  
The R<sub>f</sub> values of some 5,6-dihydroxyindoles  
on formamide-treated paper

Substance*	Average R <sub>f</sub> † in solvent:				
	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>
DHI	0	0	11	11	09
DHMI	11	23	39	49	46
DHEI	19	35	52	62	61
DHPri	29	48	64	72	72
IodoDHI	07	09	39	35	27
IodoDHMI	37	49	71	70	78
IodoDHEI	51	64	81	81	86
IodoDHPri	66	77	88	88	93

\*Code names as defined in Table I.

†R<sub>f</sub> × 100.

TABLE V  
The R<sub>f</sub> values of some 5,6-diacetoxyindoles on formamide-treated paper

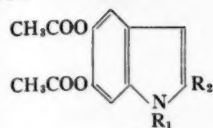
Substance*	Average R <sub>f</sub> † in solvent:				
	S <sub>8</sub>	S <sub>9</sub>	S <sub>10</sub>	S <sub>11</sub>	S <sub>12</sub>
DAI	0	0	04	60	13
DAMI	24	24	40	s.f.	77
DAEI	39	41	56	s.f.	87
DAPrI	53	57	70	s.f.	92
IodoDAI	07	09	15	79	48
IodoDAMI	47	52	63	s.f.	90
IodoDAEI	61	66	74	s.f.	93
IodoDAPrI	74	78	84	s.f.	95

\*Code names as defined in Table III.

†R<sub>f</sub> × 100.

NOTE: s.f. = the R<sub>f</sub> was very high; the substance was virtually on the solvent front.

## LE III



Colors\* with chromogenic reagents†

TPA	FHCl	Ac. ox.	Sal.‡	Nitrose	DPNA	Gib.	Xan.
OrP → P	PV → Br	Br	Or → Gy	V → PBr	RP → Br	PBr → VBr	Pr → Gy
P	PV → V	VBr	P → VBr	V → PBr	RP → Br	PBr → GyBr	V → GyV
P	PV → V	VBr	P → VBr	V → PBr	RP → Br	PBr → GyBr	V → GyV
P	PV → V	GyV	OrP → VBr	V → PBr	RP → Br	PBr → GyBr	V → GyV
P → OrP	PV → Br	VBr	GyP → GyV	PBr	V → PBr	VBr → Br	PV → GyV
P	PV → PBr	BGy	PV → GyV	GyV → PBr	V → PBr	PBr → Br	V → Gy
P	PV	BGy	PV → GyV	GyV → PBr	GyV → PBr	PBr → Br	V → Gy
P	P	Y	PV → VBr	Y → VBr	OrP → VBr	PBr → Br	V → Gy

\*First change occurs rapidly; final change occurs overnight.  
 †Color fades after 48 hours.

and the colors obtained with several reagents are given in Table III. For the purposes of  $R_f$  determination with the systems illustrated above, Ehrlich's reagent was employed to locate the zones.

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## CHARACTERISTIC VIBRATIONS OF THE SULPHURYL GROUP<sup>1</sup>

E. A. ROBINSON

### ABSTRACT

A compilation of the S—O symmetric and asymmetric stretching frequencies is given for a large number of compounds containing an —SO<sub>2</sub>— group. It is shown that a linear relationship between  $\nu_{\text{SO}_2(\text{sym})}$  and  $\nu_{\text{SO}_2(\text{asym})}$  is valid for a large number of sulphuryl and polysulphuryl compounds and that the actual frequencies depend in a systematic manner on the electronegativities of the attached groups. These relationships have proved very useful in assigning and in some cases reassigning the S—O bands in the infrared and Raman spectra of a number of sulphuryl compounds. It is pointed out that there is a relationship between the SO<sub>2</sub> frequencies of some sulphonic acids and their acid strengths.

The calculation of values for group electronegativities from the vibration frequencies of the P=O and SO<sub>2</sub> groups is discussed.

For a variety of organic compounds including sulphones, sulphonyl chlorides, covalent sulphates, sulphonamides, sulphonic acid esters, and sulphonates, the sulphur-oxygen symmetrical and antisymmetrical stretching frequencies obtained from infrared and Raman spectra have been characterized. A compilation of these frequencies has been given by Bellamy (1).

In 1957 Bellamy and Williams (2) pointed out that any change in the symmetric frequency,  $\nu_{\text{SO}_2(\text{sym})}$ , is accompanied by a proportional change in the asymmetric frequency,  $\nu_{\text{SO}_2(\text{asym})}$ . They plotted  $\nu_{\text{SO}_2(\text{sym})}$  against  $\nu_{\text{SO}_2(\text{asym})}$  for 29 compounds taken from the work of Haszeldine and Kidd (3, 4), Barnard, Fabian, and Koch (5), and of Baxter, Cymerman-Craig, and Willis (6) and obtained a good straight line. They pointed out that since the —SO<sub>2</sub>— stretching frequencies are essentially free from mass and coupling effects such a correlation is expected and that the exact positions of  $\nu_{\text{SO}_2(\text{sym})}$  and  $\nu_{\text{SO}_2(\text{asym})}$  depend on the nature of the substituents attached to the sulphuryl group. It is expected that the more electronegative the groups that are attached the stronger the S=O bonds will be and hence the higher the vibrational frequencies.

In recent years symmetric and asymmetric vibrations for sulphuryl groups in a large number of compounds including several inorganic compounds have been reported. Data for different compounds are reported in Table I and are plotted in Fig. 1. It is clear that the symmetrical and asymmetrical S—O vibrations for compounds of the type X<sub>2</sub>SO<sub>2</sub>, XYSO<sub>2</sub>, (including X(OH)SO<sub>2</sub>), for ions such as XSO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup> (although strictly speaking the S—O vibrations in these cases should not be described in this manner), and for more complex compounds containing —SO<sub>2</sub>— as part of a ring or chain, all fit the linear relationship of Bellamy and Williams (2) reasonably well.

When the —SO<sub>2</sub>— group is bonded to two alkyl groups  $\nu_{\text{SO}_2(\text{sym})}$  comes in the narrow range 1136 to 1145 cm<sup>-1</sup>, whereas for two aryl groups, or for one alkyl group and one aryl group this frequency is in the range 1150 to 1160 cm<sup>-1</sup>. In all cases  $\nu_{\text{SO}_2(\text{asym})}$  is in the range 1312 to 1334 cm<sup>-1</sup>. When an alkyl or an aryl group is replaced by the more electronegative —NH<sub>2</sub> group (e.g. in the sulphonamides), a slight shift of  $\nu_{\text{SO}_2(\text{sym})}$  and a corresponding shift of  $\nu_{\text{SO}_2(\text{asym})}$  to higher frequencies is noted;  $\nu_{\text{SO}_2(\text{sym})}$  is in the range 1152 to 1169 cm<sup>-1</sup> and  $\nu_{\text{SO}_2(\text{asym})}$  in the range 1336 to 1358 cm<sup>-1</sup>. Similarly on replacing the —NH<sub>2</sub> group by oxygen (e.g. in the sulphonic acid esters), further shifts of the S—O bands to yet higher frequencies are observed. In general, replacement of groups attached

<sup>1</sup>Manuscript received September 15, 1960.

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario.

TABLE I  
Symmetric and asymmetric vibration frequencies of the  $-\text{SO}_2-$  group\*†

	$\text{SO}_2(\text{sym})$	$\text{SO}_2(\text{asym})$		$\text{SO}_2(\text{sym})$	$\text{SO}_2(\text{asym})$
<b>Sulphonates <math>\text{RR}'\text{SO}_2</math></b>					
1. Methyl ethyl sulphone	1145	1330	(24)		
2. Dibutyl sulphone	1139	1330	(23)		
3. Methyl propyl sulphone	1139	1299-1316	(19)		
4. Diphenyl sulphone	1158	1319	(20, 24)		
5. Phenyl benzyl sulphone	1155	1325	(24)		
6. Phenyl methyl sulphone	1160	1334	(5)		
7. Dibenzyl sulphone	1155	1325	(24)		
8. Phenyl vinyl sulphone	1153	1324	(19)		
9. Methyl vinyl sulphone	1139	1312	(19)		
10. Methyl allyl sulphone	1136	1307	(19)		
11. Phenyl allyl sulphone	1150	1325	(24)		
12. $\beta$ -Chlorethyl phenyl sulphone	1156	1330	(19)		
13. Cyclohexyl methyl sulphone	1144	1321	(5)		
14. Dicyclohexyl sulphone	1130	1312	(5)		
<b>Thiolsulphonates <math>\text{RSO}_2\text{SR}</math></b>					
15. $\text{CF}_3\text{SO}_2\text{S}\cdot\text{CF}_3$	1235	1422	(20)		
16. Phenyl thiolsulphonate	1144	1331	(20)		
17. $p$ -Cyanophenyl thiolsulphonate	1154	1342	(20)		
18. $p\text{-C}_6\text{H}_4\text{CO NH}_2\text{SO}_2\text{S}\cdot\text{R}$	1154	1342	(20)		
19. $p\text{-C}_6\text{H}_4\text{C}(\text{OEt})=\text{NH}$ $\text{HCl}\cdot\text{SO}_2\text{S}\cdot\text{R}$	1154	1341	(20)		
<b>Esters of sulphonic acids <math>\text{RSO}_2\text{OR}'</math></b>					
20. Phenyl $p$ -toluene sulphonate	1170	1375	(22)		
21. 2,4-Dinitrophenyl $p$ -toluene sulphonate	1175	1355	(22)		
22. Phenoxyethyl $p$ -toluene sulphonate	1168	1350	(22)		
23. Methyl $p$ -toluene sulphonate	1185	1375	(24)		
24. $n$ -Butyl $p$ -toluene sulphonate	1185	1370	(24)		
25. Methyl methane sulphonate	1171	1358	(33)		
26. Ethyl methane sulphonate	1172	1352	(33)		
27. Methyl ethane sulphonate	1165	1356	(33)		
28. Ethyl ethane sulphonate	1170	1355	(33)		
<b>Sulphonamides <math>\text{R}\cdot\text{SO}_2\cdot\text{NH}_2</math></b>					
29. Benzene sulphonamide	1167	1358	(24)		
30. $o$ -Toluene sulphonamide	1162	1346	(24)		
31. $p$ -Toluene sulphonamide	1167	1358	(24)		
32. Sulphanilimide	1152	1337	(22)		
33. Methane sulphonamide	1169	1336	(22)		
<b>Covalent sulphates <math>(\text{RO})_2\text{SO}_2</math></b>					
34. Dimethyl sulphate	1193	1412	(17, 24)		
35. Diethyl sulphate	1187	1415	(17, 24)		
<b>Sulphonyl chlorides <math>\text{RSO}_2\text{Cl}</math></b>					
36. Methane sulphonyl chloride	1175	1370	(4, 7, 33)		
37. Benzene sulphonyl chloride	1185	1390	(24)		
38. $o$ -Toluene sulphonyl chloride	1183	1382	(4)		
39. $m$ -Toluene sulphonyl chloride	1169	1384	(4)		
40. $p$ -Toluene sulphonyl chloride	1172	1379	(4)		
41. $p$ -Chlorophenyl sulphonyl chloride	1183	1404	(4)		
42. $\text{CF}_3\text{SO}_2\text{Cl}$	1239	1439	(3)		
43. $\text{CCl}_3\text{SO}_2\text{Cl}$	1183	1404	(3)		
44. Methoxy sulphonyl chloride	1191	1404	(33)		
<b>Sulphonyl fluorides <math>\text{RSO}_2\text{F}</math></b>					
45. Methane sulphonyl fluoride	1210	1401	(7)		
46. Benzene sulphonyl fluoride	1205	1420	(7)		
47. $o$ -Toluene sulphonyl fluoride	1209	1402	(7)		
48. $m$ -Toluene sulphonyl fluoride	1203	1405	(7)		
49. $p$ -Toluene sulphonyl fluoride	1205	1412	(7)		
50. $\text{CF}_3\text{SO}_2\text{F}$	1239	1463	(4)		
<b>Acids <math>\text{XSO}_3\text{H}</math></b>					
51. $p$ -Toluene sulphonic acid	1170	—	(22)		
52. Benzene sulphonic acid	1182	—	(22)		
53. Ethane sulphonic acid	1171	—	(22)		
54. Methane sulphonic acid	1174	1354	(27)		
55. Sulphuric acid	1195	1368	(10, 12)		
56. Fluorsulphuric acid	1230	1445	(10, 12)		
57. Chlorsulphuric acid	1209	1408	(10, 12)		
<b>Inorganic sulphonyl compounds</b>					
58. Sulphuryl fluoride	1269	1501	(33)		
59. Sulphuryl chloride	1182	1414	(25)		
60. Sulphamide	1163	1350	(26)		
61. $\text{FSO}_3\text{F}$	1248	1501	(29)		
62. $\text{MeSO}_3\text{F}$	1235	1465	(30)		
63. $\text{S}_2\text{O}_6\text{F}_2$	1246	1495	(30)		



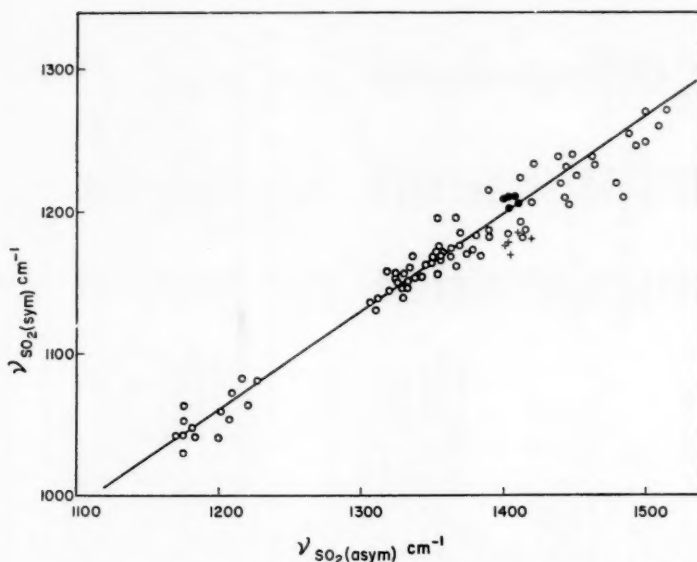


FIG. 1. Correlation of symmetric and asymmetric S—O stretching frequencies.

to the sulphuryl group by groups having a greater effective electronegativity leads to a shift in the S—O stretch to higher frequency (Table II).

The shift of the  $\text{SO}_2$  stretching frequencies to higher values as the electronegativities of the attached groups increase indicates increasing strength of the  $\text{S}=\text{O}$  bonds which

TABLE II  
Extended correlation table for S—O symmetric and asymmetric vibrations

Grouping	Type of compound	S—O	
		Symmetric	Asymmetric
C—SO <sub>2</sub> —C	Sulphone (alkyl)	1136–1145	1307–1330
	Sulphone (alkyl-aryl)	1150–1160	1325–1334
	Sulphone (aryl)		
C—SO <sub>2</sub> —N	Sulphonamide	1152–1169	1336–1358
C—SO <sub>2</sub> —O	Sulphonic acid and esters	1165–1185	1350–1375
C—SO <sub>2</sub> —F	Sulphonyl fluoride	1203–1210	1401–1412
C—SO <sub>2</sub> —S	Thiosulphonates	1144–1154	1331–1342
C—SO <sub>2</sub> —Cl	Sulphonyl chloride	1169–1185	1364–1390
N—SO <sub>2</sub> —N	e.g. Sulphamide	1163	1350
O—SO <sub>2</sub> —O	Covalent sulphates	1187–1195	1390–1415
O—SO <sub>2</sub> —F	e.g. FSO <sub>3</sub> F, HSO <sub>3</sub> F, S <sub>2</sub> O <sub>5</sub> F <sub>2</sub> , S <sub>2</sub> O <sub>6</sub> F <sub>2</sub>	1230–1260	1445–1510
O—SO <sub>2</sub> —Cl	HCISO <sub>3</sub> , S <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub> , S <sub>2</sub> O <sub>6</sub> Cl <sub>2</sub>	1205–1225	1408–1452
	Ions e.g. HSO <sub>4</sub> <sup>-</sup> , FSO <sub>3</sub> <sup>-</sup> , MeSO <sub>3</sub> <sup>-</sup>	1026–1080	1175–1221



may be reasonably attributed at least partly to increased double-bond character. The more electronegative are the groups X and Y in  $\text{XYSO}_2$  the less important are contributions from structures such as  $\text{XYS}^+\text{O}^-$  compared with the double-bonded structure  $\text{XYS}=\text{O}$ .

An example of how the above correlation of  $\nu_{\text{SO}_2(\text{sym})}$  with  $\nu_{\text{SO}_2(\text{asym})}$  and of both of these frequencies with the effect of the attached groups may be used is afforded by the sulphonyl fluorides. Bands at 1177, 1180, 1178, 1169, and 1184  $\text{cm}^{-1}$ , respectively, for methane, benzene, *o*-toluene, *m*-toluene, and *p*-toluene sulphonyl fluorides, have been assigned previously to the symmetrical stretch by Ham and Hambly (7). We suggest, however, that bands at 1210, 1205, 1209, 1203, and 1205  $\text{cm}^{-1}$ , respectively, assigned by the above workers to a vibration of the  $\text{SO}_2\text{F}$  group should be reassigned to the S—O symmetrical stretch. This vibration has a frequency in the range 1170 to 1180  $\text{cm}^{-1}$  in the corresponding chlorides and it is reasonable to expect a shift from this value to a higher value on substituting fluorine for chlorine, e.g. on passing from  $\text{SO}_2\text{Cl}_2$  to  $\text{SO}_2\text{F}_2$  the S—O symmetrical stretch shifts from 1180 to 1269  $\text{cm}^{-1}$ . Moreover the reassigned frequencies fit the straight line rather better (points indicated ● on Fig. 1) than the original assignments (indicated by + on Fig. 1).

Figure 1 also shows that for anions,  $\text{XSO}_3^-$ , the S—O bands come at much lower frequencies than for any neutral molecule. This is consistent with the smaller double-bond character of the S—O bonds in these species. The effect of the X substituent, although much reduced, is also apparent in these anions, e.g.  $\nu_{\text{SO}_2(\text{sym})}$  for  $\text{FSO}_3^-$  is at 1080  $\text{cm}^{-1}$  while this vibration has the frequency 1054  $\text{cm}^{-1}$  for  $\text{ClSO}_3^-$  and 1040  $\text{cm}^{-1}$  for  $\text{HSO}_4^-$ . The straight-line relationship between the two S—O frequencies is not so good for some of these anions possibly due to inaccuracies in the frequencies resulting from the difficulty of resolving bands in some of the spectra.

Another example of the use of the above correlation in structure determination is afforded by the observation of two bands assigned to the S—O stretches, at 1030 and 1240  $\text{cm}^{-1}$  in the spectrum of *p*-toluenesulphonic acid monohydrate. It is immediately clear from Fig. 1 that these bands are characteristic of the *p*-toluene sulphonate ion and not the parent acid so that the compound is actually the salt  $\text{H}_3\text{O}^+\cdot\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3^-$ . Again Haszeldine and Kidd (4) report the S—O bands for  $\text{CF}_3\text{SO}_3\text{H}$  at 1030 and 1176  $\text{cm}^{-1}$  but from Fig. 1 it seems that they should be assigned not to the acid but to its anion  $\text{CF}_3\cdot\text{SO}_3^-$ .

The — $\text{SO}_2$ — group frequencies in the molecule  $\text{XSO}_3\text{H}$  can be related to its strength as an acid. A similar correlation of the —OH stretching frequency in carboxylic acids with their strengths has been pointed out by Goulden (8) and the change in the carbonyl stretching frequency has been used similarly (9). The frequencies of the — $\text{SO}_2$ — symmetrical stretch in the sulphonic acids appears to increase with increasing acid strength as is shown in Table III. Disulphuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ , is a moderately weak acid of the sulphuric acid system (10). Fluorsulphuric and chloresulphuric acids are very weak acids in sulphuric acid (11) while *p*-toluene sulphonic and benzene sulphonic acids behave as weak bases of the sulphuric acid system (12) and are presumably therefore weaker acids than sulphuric acid. Comparison of  $\text{CF}_3\text{SO}_2\text{Cl}$  ( $\nu_{\text{SO}_2(\text{sym})} = 1239$ ,  $\nu_{\text{SO}_2(\text{asym})} = 1439$   $\text{cm}^{-1}$ ) with  $\text{SO}_2\text{Cl}_2$  ( $\nu_{\text{SO}_2(\text{sym})} = 1182$ ,  $\nu_{\text{SO}_2(\text{asym})} = 1414$   $\text{cm}^{-1}$ ) would suggest that the  $\text{SO}_2$  frequencies in  $\text{CF}_3\text{SO}_3\text{H}$  would be higher than in  $\text{ClSO}_3\text{H}$  and it might be predicted therefore that  $\text{CF}_3\text{SO}_3\text{H}$  would be a stronger acid than  $\text{ClSO}_3\text{H}$ . Unfortunately the

TABLE III  
Correlation of  $\nu_{\text{SO}_2(\text{sym})}$  with the acid dissociation constants  
of sulphonic acids in sulphuric acid

	$\text{SO}_2(\text{sym})$ ( $\text{cm}^{-1}$ )	$K_a$ , moles $\text{kg}^{-1}$ (25° C)
Disulphuric acid	1240	0.014
Fluorsulphuric acid	1230	0.002
Chlorsulphuric acid	1209	0.001
Sulphuric acid	1195	—
Benzenesulphonic acid	1182	Base
<i>p</i> -Toluenesulphonic acid	1170	Base

ionization of  $\text{CF}_3\text{SO}_3\text{H}$  in sulphuric acid has not been studied. It can also be predicted from a comparison of the  $\text{SO}_2$  frequencies of  $\text{CF}_3\text{SO}_2\text{F}$  at 1239 and 1463  $\text{cm}^{-1}$  and those of  $\text{FSO}_2\text{F}$  (1269  $\text{cm}^{-1}$ , 1501  $\text{cm}^{-1}$ ) that  $\text{CF}_3\text{SO}_3\text{H}$  would be a weaker acid than  $\text{FSO}_3\text{H}$ . Thus the following is probably the order of the strengths of these sulphonic acids,



A similar effect of electronegative substituents on the characteristic frequency of a group has been observed in other cases, e.g. for phosphoryl compounds (13) and for carbonyl compounds (14), and attempts have been made to devise quantitative relationships between the vibrational frequency of a group and the effective electronegativities of the attached substituents.

Bell and co-workers assumed that the  $\text{P}=\text{O}$  frequency in phosphoryl compounds is directly related to the sum of the effective electronegativities of the groups X, Y, Z, in the molecule  $(\text{XYZ})\text{P}=\text{O}$  ( $\Sigma\psi = \psi_X + \psi_Y + \psi_Z$ ). By assuming the Pauling values (4.0, 3.0, and 2.8) for the electronegativities of fluorine, chlorine, and bromine, respectively, they were able to obtain a correlation between the Raman shifts of the  $\text{P}=\text{O}$  group and the sum of the electronegativities of the halogens attached to it. The weakness of the method is that it assumes that the effect of the halogen is to be entirely attributed to its changing the effective electronegativity of the phosphorus atom and ignores any possible effects due to double-bond formation with the halogen which may be particularly important for fluorine. Generally the  $\text{P}-\text{F}$  bond distance is found to be considerably less than the sum of the covalent radii (41), and this has been attributed (15) to partial double-bond formation between fluorine and phosphorus. We find that if we consider first only the phosphoryl compounds not containing fluorine and correlate the  $\text{P}=\text{O}$  stretching frequency (Table IV) with the sum of the Pauling electronegativities in these compounds (Fig. 2), then a good straight line can be drawn which has a different slope

TABLE IV  
Values of the  $\text{P}-\text{O}$  stretching frequency in phosphoryl halides  $(\text{XYZ})\text{P}=\text{O}^*$

X	Y	Z	$\Sigma\psi^\dagger$	$\nu_{\text{P}=\text{O}}$ ( $\text{cm}^{-1}$ )	X	Y	Z	$\Sigma\psi^\dagger$	$\nu_{\text{P}=\text{O}}$ ( $\text{cm}^{-1}$ )
Cl	Cl	Cl	19.0	1290	F	F	Cl	10.2	1358
Cl	Cl	Br	8.8	1285	F	F	Br	10.0	1360
									1340/1350
Cl	Br	Br	8.6	1275	F	Cl	Cl	9.6	1331
Br	Br	Br	8.4	1261	F	Br	Br	9.2	1303
F	F	F	10.8	1395	F	Cl	Br	9.4	1319

\*Taken from Bell and co-workers (13).

†Sum of effective electronegativities ( $\Sigma\psi = \psi_X + \psi_Y + \psi_Z$ ).

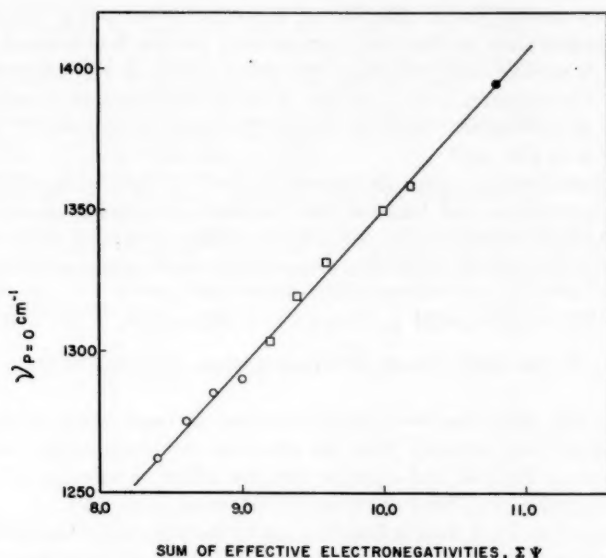
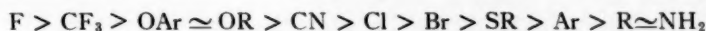


FIG. 2. Correlation of P=O stretching frequency with  $\Sigma\chi$ .  $\circ$  chloro, bromo, and chloro-bromo compounds;  $\bullet$   $\text{POF}_3$ ;  $\square$  chloro-fluoro and bromo-fluoro compounds and  $\text{POFCIBr}$ .

from the line proposed by Bell and co-workers (13). The correlation is probably justified for chloro and bromo phosphorus compounds, since the phosphorus halogen bond lengths are nearer to the sum of the covalent radii (41), indicating that the bonds are probably near to single. On the basis of the new straight line we find that a value of 3.6 is required for the effective electronegativity of fluorine in order for the P=O frequency in  $\text{POF}_3$  to fall on the straight line (Fig. 2). This can be attributed to the fact that double bonding between fluorine and phosphorus reduces the extent of P=O double bonding and thus apparently reduces the effective electronegativity of fluorine. The value 3.6 seems to be appropriate for all phosphoryl compounds since if we use this value for fluorine and the Pauling values for chlorine and bromine, then the present straight line is also found to hold for all mixed halogen-fluorine phosphoryl compounds (Fig. 2).

It is clear from the above discussion that evaluation of electronegativities for groups is complicated by the probable occurrence of double bonding. Nevertheless the order of electronegativities of groups can probably be established from the spectra. For phosphoryl compounds the order

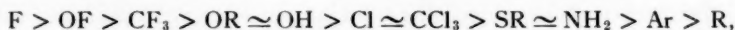


is obtained.

The multiplicity of P—F bonds implied by the low apparent electronegativity of fluorine and the short bond lengths is consistent with the P—F symmetrical stretching frequency in fluorophosphorus compounds. For the  $\text{PF}_6^-$  ion the P—F distance is apparently single (1.73 Å) and the P—F stretching frequency is at 741  $\text{cm}^{-1}$  whereas in other P—F compounds where the P—F distance is abnormally short this particular vibration is at a much higher frequency (820 to 940  $\text{cm}^{-1}$ ), implying a strengthening of the bond. In  $\text{PF}_6^-$  the outer shell contains six electron pairs and P—F double-bond

formation presumably cannot occur whereas in the other compounds considered the valency shell contains less than six electron pairs making partial double-bond formation very probable (16). A similar effect has been recognized (15), in the case of bonds of fluorine with silicon. For example, in  $\text{SiF}_4$  the Si—F bond length is 1.54 Å and the Si—F stretching frequency is at  $800\text{ cm}^{-1}$  while in  $\text{SiF}_6^-$  the bond length is 1.71 Å and the stretching frequency is at  $656\text{ cm}^{-1}$ .

In view of the obvious defects in the calculations of effective electronegativities by the method of Bell and co-workers and because few reference compounds are available no attempt has been made to evaluate the electronegativities of groups attached to the  $\text{SO}_2$  group in sulphuryl compounds. However, the order of electronegativities is probably



which is very similar to the order found for these groups attached to the phosphoryl group.

Recently Lagowski (38) using the S—O frequencies for the compounds  $\text{SO}_2\text{F}_2$ ,  $\text{SO}_2\text{Cl}_2$ ,  $\text{CF}_3\text{SO}_2\text{F}$ , and  $\text{CF}_3\text{SO}_2\text{Cl}$  has deduced that the effective electronegativity of the  $\text{CF}_3$  group is between those of fluorine and chlorine and the effect of substituted alkyl and aryl substituents on  $\nu_s$  and  $\nu_{as}$  has been discussed by Momose *et al.* (39).

Difficulties with regard to S—F double bonding are to be expected. Thus in  $\text{SF}_6$  where no double bonding between sulphur and fluorine is expected the S—F stretching frequency is at  $775\text{ cm}^{-1}$ , but in most other fluorosulphur compounds this vibration has a higher frequency in the range  $820$  to  $850\text{ cm}^{-1}$  which could be attributed to partial double-bond character of the S—F bonds.

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## NOTES

### STUDIES ON THE CRYSTALS SEPARATING FROM AQUEOUS LITHIUM NITRATE SOLUTION

G. ARAVAMUDAN\* AND S. RAMASESHAN

Systematic studies (1, 2, 3, 4) on lithium nitrate-water systems have established the existence of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ . In fact Campbell and Bailey (3c) have not only isolated this salt but have succeeded in recording its X-ray powder diagram. During the course of some investigations on  $\text{LiNO}_3\text{-H}_2\text{O}$  systems in this Institute (5) very good single crystals of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  were obtained. This note reports the determination of its space group as well as some morphological studies of anhydrous  $\text{LiNO}_3$  crystals separating from aqueous solution at various temperatures.

When an aqueous  $\text{LiNO}_3$  solution corresponding to the composition of the trihydrate (56.11%  $\text{LiNO}_3$  by weight) is cooled to  $-5^\circ\text{C}$  spontaneous crystallization occurs with the deposition of a mass of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  crystals. If one of these tiny crystals is used to inoculate a more dilute solution (50%  $\text{LiNO}_3$ ) and the temperature maintained constant (say at  $25^\circ\text{C}$ ), extremely well defined euhedral crystals, sometimes as large as  $6\text{ cm} \times 2\text{ cm} \times 1.5\text{ cm}$ , could be grown during the course of 2 days.

The crystals appeared to belong to the orthorhombic system and the peculiar distribution of the faces suggested a hemimorphic form lacking a center of symmetry (point group  $mm2$ ). The  $a$  and  $b$  faces were well developed while the  $c$  face (perpendicular to the axis of elongation) could be recognized only in rare cases. Two prominent faces which made respectively  $28^\circ$  and  $46^\circ$  with the  $b$  face were later identified as the (110) and (120) planes. These angles were measured with a contact goniometer because of the inherent difficulty of mounting these excessively hygroscopic, low-melting crystals on a two-circle goniometer.

Using a few flawless crystals the density was determined by the flotation method (bromoform + xylene mixture) to be 1.55.

Rotation and Weissenberg photographs about the  $c$  axis were taken with a single crystal enclosed in a Lindemann glass tube. The crystal belongs to the orthorhombic symmetry with unit cell dimensions  $a = 6.82\text{ \AA}$ ,  $b = 12.78\text{ \AA}$ , and  $c = 6.05\text{ \AA}$ . The observed density gave four molecules in the unit cell.

From  $hk0$ ,  $hkl$ , and  $hk2$  Weissenberg photographs it was found that the constraining condition for the appearance of  $hkl$  reflections was  $h+k = 2n$ , while that for the  $h0l$  reflections was ( $h = 2n$ ),  $l = 2n$ . All the other reflections like  $hk0$ ,  $0kl$ ,  $h00$ ,  $0k0$ , and  $00l$  were also governed by these two conditions. The only space groups consistent with these conditions are (6):

centrosymmetric space group	$Cmcm-D_{2h}^{17}$ (No. 63)
or	
non-centrosymmetric space groups	$Cmc2-C_{2v}^{16}$ (No. 40)
	$Cmc2_1-C_{2v}^{12}$ (No. 36).

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If any weight could be given to the cursory morphological examination mentioned earlier, the crystal should belong to one of the latter two non-centrosymmetric space groups. The crystal structure analysis of this substance is in progress.

A powder photograph of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  was taken using a 9-cm Unicam powder camera. Since the specimen diameter was nearly 0.6 mm, high resolution could not be attained. Table I gives an approximate visual estimate of the intensity of each line, its spacing,

TABLE I  
Powder data of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

No.	Intensity	$d$ , observed	Index	$d$ , calculated	$d$ , Campbell and Bailey
1	VW	6.40	020	6.395	6.13
2	W	6.01	110	6.015	
3	S	4.31	{ 021 111	4.358 4.268	4.20
4	W	3.40	200	3.410	3.47
5	VW	3.10	{ 040 131	3.198 3.102	
6	VS	3.01	{ 002 220	3.025 3.007	2.99
7	W	2.85	041	2.838	2.79
8	M	2.70	{ 020 112 221	2.734 2.702 2.693	2.68
9	S	2.34	{ 150 240 132	2.392 2.332 2.320	2.37
10	S	2.13	{ 222 060	2.133 2.130	2.13
11	VW	2.05	{ 061 330	2.010 2.005	2.02
12	VW	1.88	{ 331 152	1.904 1.878	1.90
13	M	1.80	212	1.800	1.80

its index, and spacing computed from the Weissenberg data as also the values reported by Campbell and Bailey. The present measurements are accurate to 1% only.

The work of Campbell and his co-workers has definitely disproved the existence of lithium nitrate hemihydrate ( $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) which Donnan and Burt (1) reported. According to these authors the anhydrous salt separating at higher temperatures (70 to 90° C) had a different crystal form from the "hemihydrate" crystals which they claimed were formed in their experiments at about 40° C. However, this suggested that the morphological study of crystals grown from concentrated aqueous solution by evaporation or by cooling at various temperatures from 0° C to 90° C would be of interest. These crystals were most carefully examined optically and goniometrically. A simple plastic attachment was made to the Unicam two-circle goniometer to completely prevent moist air from coming in contact with the hygroscopic crystals. Although the measurement of the angles were necessarily inaccurate (due to the intervening thin plastic cover) there was no doubt from the stereographic projections that all the crystals obtained were definitely the anhydrous rhombohedral  $\text{LiNO}_3$ . The crystals, however,

exhibited a profusion of faces and forms, the most prominent being  $c(0001)$ ,  $m(10\bar{1}0)$ ,  $r(10\bar{1}1)$ ,  $o(02\bar{2}1)$ ,  $e(01\bar{1}2)$ , and  $v(21\bar{3}1)$ . Measurement of the rhombohedral angle gave a value  $72^\circ 30'$  well in agreement with that computed from X-ray data (7) ( $72^\circ 42'$ ) for anhydrous  $\text{LiNO}_3$ .

It is perhaps worth while mentioning that it was impossible to separate out the trihydrate crystals from concentrated solutions of lithium nitrate even at temperatures as low as  $0^\circ \text{C}$ . Neither do these crystals form on the slow removal of water from saturated solution above  $-5^\circ \text{C}$ . This is due to the strong tendency of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  to supercool and it is precisely for this reason that seeding of the solution has to be resorted to for preparing the trihydrate crystals at ambient temperature ( $25^\circ \text{C}$ ).

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### THE FLUORINE MAGNETIC RESONANCE IN THE IONS $[\text{BF}_4]^-$ AND $[\text{BF}_3\text{CF}_3]^-$

R. D. CHAMBERS, H. C. CLARK, L. W. REEVES, AND C. J. WILLIS

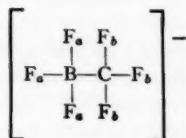
Three of the authors have recently reported the new  $[\text{BF}_3-\text{CF}_3]^-$  anion (1), the first compound with a perfluoroalkyl-boron bond. The present note presents the nuclear magnetic resonance data at 40 Mc for this ion and the  $[\text{BF}_4]^-$  ion in aqueous solution. The resonance signals were referred to an external capillary containing  $\text{CF}_3\text{COOH}$ . No corrections for diamagnetic susceptibility differences in a cylindrical tube have been employed because the magnitude of the chemical shifts observed is so large (2, 3).

At the left of the figure are shown  $\text{F}^{19}$  magnetic resonance spectra of the  $\text{CF}_3$  region of the  $[\text{CF}_3\text{BF}_3]^-$  ion (I) and the peak due to trifluoroacetic acid (II). Peak III, which is shifted  $+77.3$  p.p.m. to high field, is the  $\text{F}^{19}$  resonance of the  $\text{BF}_3$  region of the ion. The correspondence of these chemical shifts to the boron-fluorine and the carbon-fluorine electronegativity differences and the equal intensity is satisfactory proof of the formulation of the ion (4, 5). At the right of the figure the spectrum of the  $[\text{BF}_4]^-$  ion is shown from a concentrated aqueous solution of the sodium salt. Chemical shifts are indicated above the respective spectrum.

The spectra all show a quartette with some underlying structure which is not resolved.

This quartette arises from indirect spin-spin interaction between the 81.2% abundant  $B^{11}$  isotope and  $F^{19}$ . It is to be noted that the individual multiplets are much narrower in the  $[BF_4]^-$  ion because the tetrahedral symmetry minimizes the electric field gradients at the boron nucleus (6, 7, 8).

The spectrum of the  $[BF_3-CF_3]^-$  ion should reflect the following coupling constants  $J_{B^{11}-F_a^{19}}$ ,  $J_{B^{11}-F_b^{19}}$ , and  $J_{F_a^{19}-F_b^{19}}$  from



The values obtained are  $J_{B^{11}-F_b^{19}} = 34$  c.p.s.,  $J_{B^{11}-F_a^{19}} = 39.0$  c.p.s., and  $J_{F_a^{19}-F_b^{19}}$  is not resolved. The value of  $J_{B^{11}-F_a^{19}}$  is similar to that observed in  $BF_3$  (6). In the  $[BF_4]^-$  ion  $J_{B^{11}-F^{19}}$  is only 4.8 c.p.s.

The spectrum for the  $[BF_4]^-$  shows that no other species such as  $[BF_3(OH)]^-$  is present in any appreciable amount, in agreement with the observations of Wamser (9) that the degree of hydrolysis of  $[BF_4]^-$  in concentrated solutions is very small. It has already been found that the  $[CF_3BF_3]^-$  ion is not appreciably hydrolyzed in aqueous solution (1) and the simple N.M.R. spectrum found is therefore to be expected, in the absence of species such as  $[CF_3BF_2OH]^-$ .

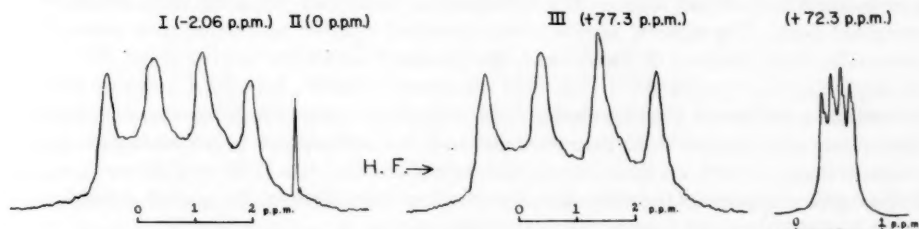


FIG. 1.

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REARRANGEMENT IN THE REACTION BETWEEN THIONYL CHLORIDE  
AND 3-METHYL-2-BUTANOL

C. C. LEE AND A. J. FINLAYSON

Nucleophilic displacements which occur with retention of configuration have been designated  $S_Ni$  reactions (1). The most extensively studied reaction of this type is that between thionyl chloride and secondary alcohols. Recent work in this field has led to the conclusion that  $S_Ni$  reactions possess considerable ionic characteristics, with carbonium ions or ion-pairs suggested as intermediates (2-5). Rearrangements typical of intermediate carbonium ions have been observed by Cram (2) for the reaction of thionyl chloride with the stereoisomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol, and 3-phenyl-2-pentanol. The present communication reports the formation of a rearranged product from the reaction between thionyl chloride and 3-methyl-2-butanol.

3-Methyl-2-butanol was added dropwise, with stirring, to a 100% excess of purified thionyl chloride at  $-35^\circ\text{C}$ . Stirring was continued for 2 hours at  $-35^\circ\text{C}$ . The hydrogen chloride produced was pumped off at about 25 mm pressure. The reaction mixture was then allowed to stand at room temperature for 1.5 hours before the excess thionyl chloride was distilled at  $29-31^\circ\text{C}$  at 25-30 mm. The resulting chlorosulphite was decomposed by heating at  $40-50^\circ\text{C}$  for 1.5 hours. Evolution of sulphur dioxide was noted during the decomposition. On raising the temperature, the crude product distilled. The distillate was washed with water and with dilute sodium carbonate solution until the washing remained basic. The washed product was dissolved in ether and dried over phosphorus pentoxide. After removal of the solvent, the residue was distilled to give about 20% yields of alkyl chloride, b.p.  $84-85^\circ\text{C}$  (lit. (6a) for *t*-amyl chloride, b.p.  $86^\circ\text{C}$ ), which gave an immediate precipitate with alcoholic silver nitrate at room temperature. The infrared absorption spectrum of this product showed all the absorption peaks as known *t*-amyl chloride together with an extra, weak and broad band in the  $1725$  to  $1750\text{ cm}^{-1}$  region. These results appear to indicate that the reaction product may be *t*-amyl chloride contaminated with a small amount of unknown impurity.

To confirm the identity of the reaction product as chiefly *t*-amyl chloride, it was converted to the Grignard reagent followed by reaction with carbon dioxide to give dimethyl-ethylacetic acid (7, 8) with an over-all yield of 35%. The low yield was to be expected since it is difficult to prepare Grignard reagents from *t*-alkyl halides. The dimethyl-ethylacetic acid was identified by conversion to the *p*-phenylphenacyl ester, which melted alone and on admixture with an authentic sample at  $84^\circ\text{C}$  (lit. (6b) m.p.  $86.5^\circ\text{C}$ ). Considering these results, it is reasonable to conclude that *t*-amyl chloride was obtained from the reaction of thionyl chloride with 3-methyl-2-butanol. A 1,2-hydride shift must have occurred in the reaction. A similar type of 1,2-shift has been noted in the reaction of thionyl chloride with 2-butanol-1- $\text{C}^{14}$ , resulting in the formation of some 2-butyl-4- $\text{C}^{14}$  chloride.\* The rearrangement in the labelled 2-butyl system was found to occur during the  $S_Ni$  reaction itself and did not arise during the process of purification or degradation. With these findings in mind, it appears safe to conclude that the *t*-amyl chloride obtained in the present study actually resulted from rearrangement during the reaction between thionyl chloride and 3-methyl-2-butanol. Rearrangements resulting from 1,2-shifts in the 3-methyl-2-butyl system have also been noted in carbonium ion-type reactions

\*Unpublished work of C. C. Lee and D. G. Lee.



(9, 10). The present finding, therefore, supports the suggestion that reactions of thionyl chloride with secondary alcohols involve ionic intermediates.

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#### SYNTHESIS OF $\alpha$ -POLYOXYMETHYLENE- $C^{13}$ AND $\alpha$ -POLYOXYMETHYLENE- $O^{18}$ \*

R. N. RENAUD AND L. C. LEITCH

Several methods of preparing formaldehyde labelled with  $C^{14}$  have been proposed (3). In all these syntheses the aldehyde is obtained as an aqueous solution. An earlier paper on the synthesis of deuterated formaldehyde by one of us (1) indicated the difficulty of obtaining polymeric formaldehyde from such solutions. Nevertheless, according to Jones and Skraba (2), evaporation of an aqueous solution obtained by hydrolysis of chloromethyl- $C^{14}$  acetate leaves a residue of dry formaldehyde- $C^{14}$  polymer. In our experience only traces of polymer were ever obtained under these conditions. Consequently, polyoxymethylene- $C^{13}$  was prepared from chloromethyl- $C^{13}$  acetate by a modification of the procedure employed in making deuterated polymeric formaldehyde. When a solution of chloromethyl- $C^{13}$  acetate in benzene is heated with the calculated amount of water the ester is slowly hydrolyzed to formaldehyde- $C^{13}$ , which is deposited as  $\alpha$ -polyoxymethylene of melting point 168–170° C on the wall of the condenser in 77% yield.

The chloromethyl- $C^{13}$  acetate was prepared by chlorinating methyl- $C^{13}$  acetate by means of sulphuryl chloride and a trace of peroxide instead of elemental chlorine as described by Jones and Skraba (2). In this way formation of the dichloroester is almost entirely suppressed. The methyl- $C^{13}$  acetate was prepared by heating methyl- $C^{13}$  iodide and silver acetate in a sealed tube.

Polyoxymethylene labelled with  $O^{18}$  was prepared by heating the normal compound with water containing approximately 20% excess  $O^{18}$  and a trace of sulphuric acid. The product isolated from the reaction analyzed 9%  $CH_2O^{18}$ . Hydrolysis of chloromethyl acetate with  $H_2O^{18}$  gave polyoxymethylene, which contained only 2.7%  $CH_2O^{18}$ .

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## EXPERIMENTAL

*Methyl-C<sup>13</sup> Acetate*

Silver acetate (21.0 g, 0.125 mole) was placed in a high-pressure glass tube which was constricted near the top to facilitate sealing later and attached to the vacuum line. The salt was dried at 80° for 4 hours by continuous pumping. Methyl-C<sup>13</sup> iodide (14.3 g, 0.1 mole) containing 24% excess C<sup>13</sup> was distilled into the tube of silver acetate, which was then sealed off at the constriction. The tube was heated in a rocking furnace for 24 hours at 90–100° C. It was then cooled in dry ice, opened, and attached to the vacuum line. Volatile products were distilled from the silver iodide into another trap on the vacuum line. Yield, 7.6 g (theoretical amount). Fractional distillation in a small column packed with glass helices gave 6.4 g of methyl-C<sup>13</sup> acetate, b.p. 56.2–56.4° C. Yield, 84%.

*Chloromethyl-C<sup>13</sup> Acetate*

Methyl-C<sup>13</sup> acetate (6.4 g, 0.08 mole) and 0.15 g of dibenzoyl peroxide were placed in a small flask with a side arm carrying a separatory funnel. The neck of the flask was surmounted by a condenser and a spiral trap cooled to –78° in dry ice and acetone. A drying tube filled with Drierite was attached to the open end of the trap. Freshly distilled sulphuryl chloride (13 g, 0.1 mole) was added very slowly to the methyl-C<sup>13</sup> acetate, which was heated just below its boiling point. The progress of the reaction was followed by observing the volume of liquid in the trap. It took 2 days to complete the reaction. When the reaction mixture is heated too rapidly free chlorine begins to appear in the trap. The rate of the reaction is considerably reduced by traces of methyl iodide, which acts as a peroxide inhibitor.

The reaction mixture was placed on the vacuum line, freed of dissolved hydrogen chloride and sulphur dioxide, and distilled into another trap on the line. The distillate obtained was fractionated in a column packed with glass helices to give 5.2 g of product, b.p. 114° C (70% of the theoretical amount).

*Polyoxymethylene-C<sup>13</sup>*

Chloromethyl-C<sup>13</sup> acetate (5.2 g, 0.05 mole) in 10 ml of benzene was added all at once to a mixture of 20 ml of benzene, 0.9 ml of water, and one drop of concentrated sulphuric acid in a 50-ml three-necked round-bottomed flask equipped with a thermometer, an inlet tube for passing in nitrogen, a stirring bar, and a reflux condenser. A Stock trap cooled to –78° in dry ice and acetone was connected to the condenser. The reaction mixture was gradually heated to 65–70° C while a slow current of nitrogen was passed through it. Rapid stirring is required to keep the water suspended in the benzene. After 7 hours' heating and stirring, white polymeric material began to appear on the wall of the condenser. After another 8 hours the flask was removed from the condenser and replaced by a plug. Liquid in the condenser was pumped away and the hard white solid scraped off. It was washed with a little absolute ether and dried. Yield, 0.3 g. By replacing the flask with the reaction mixture and resuming heating and stirring for another 10 hours, more polymer was obtained. The total yield of product isolated was finally 1.1 g (77% of the theoretical). This product melted at 169–171° C and analyzed 24% excess C<sup>13</sup> by mass spectrometry. There was 1% of an unknown impurity of mass 61.

*Polyoxymethylene-O<sup>18</sup>*

A mixture of 0.5 g of polyoxymethylene, 20 ml of benzene, 5.5 ml of water containing 20% excess O<sup>18</sup>, and a drop of concentrated sulphuric acid was heated for 24 hours in a sealed tube at 80° C. The contents of the tube were then transferred to the apparatus

used to prepare the  $C^{13}$ -labelled compound and heated as described in that preparation. A small amount of polymer, m.p. 145–150° C, which contained 9.5%  $CH_2O^{18}$  was isolated.

Hydrolysis of chloromethyl acetate with  $H_2O^{18}$  and a trace of sulphuric acid under the conditions used to prepare polyoxymethylene- $C^{13}$  gave a polymer which contained only 2.73%  $CH_2O^{18}$ . This is what would have been expected from our knowledge of the hydrolysis of esters in  $H_2O^{18}$ . The presence of the small amount of  $CH_2O^{18}$  is due to exchange.

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